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CONTENTS.

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

* The year is not inserted in references to 1918.

ABBREVIATED TITLE	JOURNAL.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Bd. Agric.	Journal of the Board of Agriculture
J. Chem. Ind., Tokyo.	Journal of Chemical Industry, Tokyo.
J. Exp. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Immun.	Journal of Immunity.
J. Ind. Eng Chem.	Journal of Industrial and Engineering Chemistry.
J. infec. Dis.	Journal of infectious Diseases.
J. Landw.	Journal fur Landwirtschaft
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J Pharm Expt Ther.	Journal of Pharmacology and Experimental Therapeutics
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.
J. pr. Chem.	Journal fur praktische Chemie
J. Röntgen Soc.	Journal of the Röntgen Society.
J. Roy. Agric. Soc	Journal of the Royal Agricultural Society.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Tokyo Chem. Soc.	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid Zeitsch.	Kolloid Zeitschrift.
Krakauer Anz.	Krakauer Anzeiger.
Lancet	The Lancet.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden fran Kongl. Vetenskapsakademiens Nobel-Institut.
Mem. Coll. Sci. Kyōtō	Memoirs of the College of Science, Kyōtō Imperial University.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften
Mon Sci.	Moniteur Scientifique.
Month. Not. Roy. Astr. Soc.	Monthly Notices of the Royal Astronomical Society, London.
P.	Proceedings of the Chemical Society.
Pflüger's Archiv.	Archiv fur das gesammte Physiologie des Menschen und der Thiere.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift
Physiol. Abstr.	Physiological Abstracts.
Physiol. Research	Physiological Research.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc. London.	Proceedings of the Physical Society of London.
Proc Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. exp. Physiol.	Quarterly Journal of Experimental Physiology.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.

ABBREVIATED TITLE.	JOURNAL.
Soi. Sci.	Soil Science
T.	Transactions of the Chemical Society
Trans. Faraday Soc.	Transactions of the Faraday Society
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada
Wien. Med. Woch.	Wiener Medizinische Wochenschrift.
Zeitsch. anal. Chem.	Zeitschrift fur analytische Chemie
Zeitsch. angew. Chem.	Zeitschrift fur angewandte Chemie
Zeitsch. anorg. Chem.	Zeitschrift fur anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift fur Elektrochemie
Zeitsch. Nahr.-Genussm.	Zeitschrift fur Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. offentl. Chem	Zeitschrift fur offentliche Chemie.
Zeitsch. physikal. Chem	Zeitschrift fur physikalische Chemie, Stochiometrie und Verwandtschaftslehre
Zeitsch. physiol. Chem.	Hoppe-Seyler s Zeitschrift fur physiologische Chemie.
Zeitsch. wiss. Photochem.	Zeitschrift fur wissenschaftliche Photographie, Photophysik und Photochemie.
Zentr. Physiol.	Zentralblatt fur Physiologie.
Zentr. Zuckerind.	Zentralblatt fur Zuckerindustrie

ANNUAL REPORTS

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

THE publication of original work falling within the purview of this section of the Annual Reports has undergone further restriction during 1918. Although it would be rash to assume that the low-water mark has been reached, it is to be hoped that the demobilisation of chemists engaged on war work will be quickly followed by a revival of activity in the investigation of the many non-technical physico-chemical problems which call for inquiry. It is true that a number of valuable researches have been published during the year, but the general paucity of the literature has made the writing of a connected Report a somewhat difficult matter. Shortage of paper and the high cost of printing have had to be considered to some extent in connexion with the publication of scientific memoirs, and, as announced in last year's Report, the *Zeitschrift für physikalische Chemie* was to have been discontinued on account of paper shortage. Unexpected supplies must have come to hand, however, for the projected temporary disappearance of this journal does not seem to have been carried into effect.

The Atomic Number Hypothesis.

The idea that the weights of the atoms are of fundamental significance in connexion with the formulation of the functional relations which are embodied in the periodic system has come to be regarded almost as axiomatic, and it is not surprising that there should be some reluctance in the acceptance of the view that the fundamental parameter is the atomic number.

The significance of the atomic number has been discussed in a

series of papers [1] by H. S. Allen, who has brought forward a considerable amount of evidence in support of the existence of a simple relation connecting the atomic number N and the characteristic atomic frequency ν, which may be written in the form $N\nu = n\nu_A$ or $N\nu = (n + \frac{1}{2})\nu_A$, where n represents an integer and ν_A the fundamental atomic frequency which is equal to $21 \cdot 3 \times 10^{12} (\text{sec.}^{-1})$.

In considering the application of this equation to the elements, it is essential that the inadequacy of the methods at our disposal for the determination of the characteristic frequencies should be kept in mind, but having due regard for this circumstance, and also for the fact that elements of high atomic number afford little evidence for or against the assumed relation, it must be admitted that the idea of a fundamental atomic frequency is supported by a substantial array of evidence. Considered in reference to the theory of probability, it has been shown that the chance of the relation being accidental is very small. When the alternative series of atomic numbers proposed by Moseley (lithium, $N = 3$) and by Rydberg (lithium, $N = 5$) are examined in reference to the above equations, the result is found to be in favour of the Moseley series.

Considerations of the same kind have been applied [2] to compound substances, the molecular number of a compound $A_a B_b C_c$ being given by the equation $N = aN_a + bN_b + cN_c$, in which N_a, N_b, and N_c are the atomic numbers of the component elements. For compound substances, the characteristic frequency may be calculated [3] from the specific heat at low temperatures, from Lindemann's formula, or from the wave-lengths of the residual rays investigated by Rubens. The available data for both inorganic and organic compounds furnish evidence in support of the relation between N and ν, and the concordance is such that it can scarcely be regarded as fortuitous. The fact that the equation holds for inorganic compounds, which include elements belonging to all the different groups of the periodic table,[4] suggests that it is the expression of a relation which is characteristic of all substances in the solid state.

Atomic Structure and High Frequency Spectra.

In agreement with the view that the entities concerned in the emission of high frequency spectra are subatomic in character,

[1] *Proc. Roy. Soc.*, 1917, [A], **94**, 110; *A.*, ii, 191. Compare also *Ann. Report*, 1917, 4.

[2] H. S. Allen, *Phil. Mag.*, 1918, [vi], **35**, 338; *A.*, ii, 163.

[3] *Ibid.*, 404; *A.*, ii, 191.   [4] *Ibid.*, 445; *A.*, ii, 225.

frequent attempts have been made to interpret these spectra in terms of the Rutherford model atom and the Bohr theory of emission. According to P. Debye[5] and L. Vegard,[6] the K series of lines is most probably due to an inner ring of three electrons, although, according to the latter, it would be possible to explain the emission of these lines in terms of a four-membered ring. The L, l, and M series of lines are supposed by Vegard to be due to rings of electrons, which require more than one energy quantum for their disturbance, and it is suggested that the source of the L series is a seven-membered ring requiring two quanta for the removal of one of the constituent electrons. Similarly, the l and M series are attributed to eight- and nine-membered rings, which require, respectively, two and three quanta for the removal of an electron. In accordance with these views, the same author[7] has devised models for the whole of the known elements, and it is claimed that these afford a satisfactory account of the periodicity in their properties. With increasing atomic number, there is a gradual increase in the number of the concentric rings, but each ring is said to retain its individual characteristics throughout the entire series of elements. These characteristics are the number of the constituent electrons and the number of energy quanta which are required for the dislocation of the ring by the removal of an electron. In general, the number of quanta increases with the diameter of the ring.

The question of the connexion between the high frequency spectra and the structure of the atoms is also discussed by Sommerfeld[8] and by Kroo,[9] the latter of whom claims to show that experimental observations are in favour of the view that the innermost ring contains three, and the next ring eight, electrons.

For the most part, the design of model atoms has been mainly concerned with the interpretation of physical properties, and little attention has been paid to the chemical properties of the elements. In a recently suggested structure,[10] due regard has been paid to the necessity of explaining those changes in valency which are produced by chemical means, as distinguished from those which are the result of α- and β-ray processes. In this model atom, there is a central negative core in which the β-ray electrons travel in closed orbits. Positive electrons move in orbits which closely surround the negative core, and outside these are the negative

[5] *Physikal. Zeitsch.*, 1917, **18**, 276 ; *A.*, 1917, ii, 434.

[6] *Ber. Deut. physikal. Ges.*, 1917, **19**, 328 ; *A.*, ii, 93.

[7] *Ibid.*, 344 ; *A.*, ii, 94.

[8] *Physikal. Zeitsch.*, 1918, **19**, 297 ; *A.*, ii, 303.

[9] *Ibid.*, 307 ; *A.*, ii, 303.

[10] A. W. Stewart, *Phil. Mag.*, 1918, [vi], **36**, 326 ; *A.*, ii, 395.

valency electrons, which move in elongated, elliptical orbits comparable with those of comets in the solar system. It is suggested that when these electrons are in a position of aphelion to the nucleus, the relatively slow movement and the small attraction exerted by the nucleus will make them periodically less resistant to the action of forces which tend to remove them from the atom. Elliptical orbits of considerable eccentricity are thus supposed to furnish the recurrent conditions of instability which are favourable to chemical changes of valency.

Amongst other model atoms which have attracted attention are those in which a pyramidal structure is assumed, the atom consisting of a nucleus, a ring of electrons in the form of a circle the axis of which passes through the nucleus, and a single stationary electron on this axis. The investigation of the dynamical stability of such systems has shown [11] that no positively charged or neutral atom can be of this type, and that the structure is incompatible with a steady rotation of the ring electrons. The molecular structures which have been formulated, in particular by Stark, would seem to be vitiated by this proof of the dynamic instability of pyramidal atoms.

Emission Spectra.

The success achieved by Bohr's theory in its interpretation of the series line spectrum of hydrogen has been in no small way responsible for the attention which has been given to this author's view of the structure of the hydrogen atom. The closeness of the agreement between the observed and calculated wave-lengths is indeed remarkable, but the fact should not be overlooked that Bohr's model atom does not suffice for the explanation of other emission effects which are associated with hydrogen. The passage of hydrogen canal rays through hydrogen or oxygen is accompanied by the emission of an ultra-violet continuous spectrum which appears to be characteristic of hydrogen.[12] The radiating entity is neither the hydrogen ion nor the neutral atom, and it is suggested that the emission may be due to an intermediate phase in which the ion is loosely associated with an electron. Whatever the real nature of this may be, the canal ray observations are said to show definitely that the carrier contains a single atom of hydrogen. In these circumstances, Stark contends that Bohr's model only furnishes an incomplete picture of the structural relations. Bohr's model of the hydrogen molecule is called into question [13] on similar grounds, in that it fails to provide an explana-

[11] J. W. Nicholson, *Proc. Physical Soc. London*, 1918, **30**, 65 ; *A.*, ii, 163.

[12] J. Stark, M. Görcke, and M. Arndt, *Ann. Physik.*, 1917, [iv], **54**, 81 ;
A., ii, 141.   [13] J. Stark, *ibid.*, 111 ; *A.*, ii, 141.

tion of the facts which have led Stark to the conclusion that the many-lined spectrum of hydrogen is attributable to diatomic aggregates carrying a single positive charge.

Attempts to determine the distribution of intensity amongst series lines under varying conditions of excitation have given results which are not very concordant, and this is attributed to sources of error introduced by the method of excitation employed. Greater consistency is claimed[14] for the results obtained with cathode rays as the exciting agent, and from observations on the Balmer series it is found that the relative intensities of the lines are independent of the current strength and also of the potential difference, whilst on the other hand the lines of longer wave-length become relatively more intense as the pressure of the hydrogen is increased. The pressure influence is not observed when the increase of pressure is brought about by the admixture of other gases with the hydrogen. Similar pressure effects have been met with[15] in the investigation of the line and band spectra emitted by nitrogen, neon, and helium.

When glow discharge is allowed to take place through a tube containing a mixture of elementary gases, the character of the emission varies from point to point of the positive column, and this variation is apparently determined by the distribution of the spectra of the constituent gases along the region of the discharge. In proceeding from the cathode towards the anode, the order in which the spectra make their appearance is the same as that of the elements arranged according to increasing ionisation potential.[16] In a mixture of mercury, nitrogen, and argon, the spectrum of mercury appears first and that of argon last, and this is the order of the ionising potentials.

In reference to the spectra of isotopes, evidence was recently brought forward[17] in support of the view that the wave-lengths of the high-frequency lines are identical. More recently, the spectra of ordinary lead and of lead from radium (radium-G) have been examined, and from observations[18] on the line λ 4058, which appear to have been carried out with great care, it would seem that there is a difference of about 0·0043 Å. in the wave-lengths of the lines emitted by the two isotopes.

The spectral examination of a large number of meteorites has

[14] J. Holtsmark, *Ann. Physik.*, 1918, [iv], **55**, 245 ; *A.*, ii, 283.

[15] L. Hamburger, *Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1043 ; *A.*, ii, 210.

[16] O. Hardtke, *Ann. Physik.*, 1918, [iv], **56**, 383 ; *A.*, ii, 385.

[17] *Ann. Report*, 1917, 3.

[18] W. D. Harkins and L. Aronberg, *Proc. Nat. Acad. Sci.*, 1917, **3**, 710 ; *A.*, ii, 89.

shown [19] that these are very similar in respect of their qualitative composition. The fact that only ten of the known elements—iron, chromium, magnesium, nickel, silicon, sodium, manganese. potassium, aluminium, and calcium—are present is somewhat remarkable and suggests that the aerolites have a common origin in the disruption of some stellar body, for which the process of cosmical evolution is complete. The siderites appear to be of different origin.

Some of the older problems connected with the interpretation of flame spectra are recalled by the publication of results [20] obtained in a direct comparison of the flame and furnace spectra of iron. Between 1500°, at which the furnace spectrum is first observed, and 2400°, the flame spectra are identical with the furnace spectra at corresponding temperatures. At higher temperatures, the furnace spectrum shows a series of bright lines, which appear to be due to the passage of a current through the vapour of the metal, for when the possibility of electrical action is excluded, the line spectrum disappears. [21] It is noteworthy that this line spectrum is shown by the inner cone of an air–coal gas flame, and that the temperature of the emitting zone is less than 1700°. Some of the lines are also found in the spectrum of an oxy-acetylene flame at about 2700°, but their intensity is very much less than that of the lines in the spectrum of the Bunsen inner cone. This cone spectrum shows, in fact, an approximation to that of the self-induction spark. The observations seem to show that conditions favourable to the emission of the line spectrum of iron may be produced either by chemical or electrical actions, but not at all readily by purely thermal action.

Fluorescence Spectra.

The fluorescence exhibited by inorganic salts when subjected to bombardment by high-speed cathode rays is characterised by the emission of the series lines of the metal, and for different salts of the same metal the energy required to produce the effect increases with the heat of formation of the salt. The series lines are also emitted when the salts are bombarded by canal rays, but in this case the critical exciting energy varies but little with the electro-negative constituent of the salt. Experiments [22] made with canal rays show that the transition from the non-fluorescent to the fluorescent condition is accompanied by a sudden diminution in

[19] Sir W. Crookes, *Phil. Trans.*, 1917, [A], **217**, 411 ; *A.*, ii, 25.
[20] G. A. Hemsalech, *Phil. Mag.*, 1918, [vi], **36**, 209 ; *A.*, ii, 341.
[21] *Ibid.*, 281 ; *A.*, ii, 384.
[22] S. E. Ohlon, *Ber. Deut. physikal. Ges.*, 1918, **20**, 9 ; *A.*, ii, 285.

the positive current attributable to the production of metal ions by the action of the canal rays on the salt molecules. In spite of the above-mentioned difference, it would seem, therefore, that the carriers are the same for both cathode-ray and canal-ray fluorescence.

Resonance Spectra.

The resonance spectra, emitted by the vapour of iodine subjected to the action of the green and yellow mercury lines have been further examined,[23] with the result that the doublet series excited by the green line has been traced to the doublet of the twenty-seventh order. This apparently represents the limit of the resonance spectrum, which thus terminates at about the same point as the absorption spectrum of iodine vapour. The frequency difference between the components of the doublets is found[24] to be constant, and the spacing of the doublets in the series representable by the equation

$$1/\lambda_m = 183075 - 2131 \cdot 414m + 12 \cdot 734m(m-1)/2,$$

where λ_m is the wave-length of the first member of the doublet of the mth order.

Absorption Spectra.

Considérable attention has been given to the question of the connexion between chemical constitution and light absorption. According to A. Hantzsch[25] the absorptive capacity of a dissolved substance is not seriously modified by the formation of additive compounds with the solvent, a circumstance which has a parallel[26] in the absence of any marked change in absorption when the degree of association (polymerisation) of the molecules of the dissolved substance is subjected to alteration. In other words, the general nature of the absorption is not affected to any large extent by the formation of molecular compounds, whether the components of these are like or unlike, provided that the process is not accompanied by a change in molecular constitution. Such cases require to be sharply distinguished from those in which the absorption varies considerably with the nature of the solvent. Substances that exhibit this behaviour are to be regarded as undergoing a change in constitution, the extent of which depends on the nature of the solvent medium. Tautomeric substances afford the best known examples of this class.

[23] R. W. Wood, *Phil. Mag.*, 1918, [vi], **35**, 236; *A.*, ii, 90.
[24] R. W. Wood and M. Kimura, *ibid.*, 252; *A.*, ii, 91.
[25] *Ber.*, 1917, **50**, 1413; *A.*, ii, 2.
[26] A. Hantzsch and E. Scharf, *ibid.*, 1913, **46**, 3570; *A.*, 1914, ii, 5.

Excluding those cases in which chemical reaction occurs between solute and solvent, with the formation of new substances, Hantzsch considers that genuine solvent action, whether accompanied or not by the formation of solvates, has no direct influence on the optical behaviour of the solute. Indirectly, the optical properties may be affected by the solvate formation in that the equilibrium between the tautomeric forms of a substance may be displaced by changes in the relative stability of the corresponding solvates.

The relations exhibited by the absorption spectra of the organic acids, salts, and esters are not by any means satisfactorily accounted for by the structural formulæ usually assigned to these substances. The alkali and alkaline earth metal salts of a given fatty acid are optically identical, and the same is true of the alkyl esters, but the esters always exhibit greater absorption than the salts, and the free acids commonly occupy an intermediate position. The differences in question are presumably due to constitutive differences, and from the optical data the conclusion [27] has been drawn that whilst the alkyl groups in the esters are attached to an oxygen atom in the usually accepted manner, the ionisable atoms of the acids and salts are attached to both oxygen atoms, as represented by the formula $R_3C \cdot C{<}^{O}_{O}{\}}H(M)$. This distinction between the acids and their esters affords, moreover, some explanation [28] of the relative ease with which the hydrogen of the acid is removed by electrolytic dissociation.

The group of nitrates also shows marked optical differences. Whilst the nitrates of the strongly electro-positive metals exhibit selective absorption in the ultra-violet, the organic nitrates cut off the ultra-violet end of the spectrum completely. The difference cannot be attributed [29] to ionisation or to hydration, but seems to indicate a difference in the constitution of the NO_3-group in the two classes of compounds. The absorption of fused potassium nitrate resembles closely that of solutions of the alkali nitrates and differs notably from the non-selective absorption of anhydrous nitric acid, which thus appears to have the constitution of the esters. On the other hand, the addition of increasing quantities of water to the anhydrous acid is accompanied by a gradual change in the absorption from the ester type to the type which is exhibited by the alkali metal salts. In the form of vapour,[30] nitric acid behaves

[27] A. Hantzsch, *Ber.*, 1917, **50**, 1422 ; *A.*, ii, 4.

[28] A. Hantzsch, *Zeitsch. Elektrochem.* 1918, **24**, 201 ; *A.*, ii, 299.

[29] K. Schaefer and H. Niggemann, *Zeitsch. anorg. Chem.*, 1916, **97**, 285 ; *A.*, 1917, ii, 61.

[30] K. Schaefer and S. Deichsel, *ibid.*, 1916, **98**, 70 ; *A.*, 1917, ii, 186.

optically like the anhydrous acid, and the addition of concentrated sulphuric acid[31] to an aqueous solution of nitric acid tends to transform the absorption into the ester type. The optical properties of the nitrates of the less electro-positive metals[32] show a diversity of behaviour which cannot be adequately explained in terms of the two differently constituted forms which seem to be indicated by the above observations, although there appears to be some connexion between the absorption and the electro-affinity of the metal. Observations of this kind indicate that the absorption affords a delicate means of detecting constitutional differences which are not indicated by other methods, thereby facilitating the differentiation of substances which belong to the same chemical group.

Interesting results have also been obtained in the investigation of solutions of bismuth chloride[33] by the absorption method.

Electrical Conductance. Ionisation.

In a criticism of the Kohlrausch method for the determination of the electrical conductivity of solutions, it is pointed out that a number of assumptions are involved which have not yet been submitted to the test of experiment, and a new method is described[34] in which the doubtful factors are avoided. In this, the conducting solution is traversed by a direct current, the effect of polarisation at the electrodes being completely eliminated by a modification of the procedure followed in the measurement of the resistance of a metallic conductor, the fall of potential in the conductor being determined when this is traversed by a known current. For N-silver nitrate, the method gives results in agreement with the values obtained by the Kohlrausch method, but for N-hydrochloric acid and N-sulphuric acid the results given by the direct-current method are, respectively, 0·3 per cent. greater and 3·6 per cent. less than the numbers furnished by the alternating-current method.

The increased accuracy attainable in conductivity measurements by recent improvements[35] in the Kohlrausch method has led to a reinvestigation of the conductance of very dilute solutions of electrolytes.

The question of the nature and magnitude of the water correc-

[31] K. Schaefer and H. Niggemann, *Zeitsch. anorg. Chem.*, 1916, **98**, 77; *A.*, 1917, ii, 186.

[32] K. Schaefer, *Zeitsch. wiss. Photochem.*, 1918, **17**, 193; *A.*, ii, 254.

[33] K. Schaefer and F. Hein, *Zeitsch. anorg. Chem.*, 1917, **100**, 249; *A.*, ii, 1.

[34] E. Newbery, *T.*, 1918, **113**, 701.   [35] Compare *Ann. Report*, 1917, 10.

tion, and of the influence of carbonic acid and the products to which this gives rise by metathesis, are critically examined,[36] and attention is directed to the necessity of using purer samples of water and of eliminating the influence of carbonic acid by measurements out of contact with the air. A simple method for the preparation of "ultra-pure" water is described[37] in which ordinary conductivity water is heated to near its boiling point in a quartz still in a current of carefully purified air, the water vapour being condensed in a block-tin tube and collected in a quartz receiver. The conductivity of the condensate varies from $0·05$ to $0·07 \times 10^{-6}$ mho at $18°$.

In this connexion, the extrapolation of conductivity data to zero concentration has been considered. The methods previously employed are regarded as untrustworthy, and a new mode of procedure is described[38] which consists in plotting $ca^2/(1-a)$ against c for a series of assumed values of Λ_∞, and rejecting such values of Λ_∞ as cause the curve to exhibit radical changes in direction in the region of very dilute solution. It is claimed that in this way Λ_∞ may be determined with an accuracy of $\pm 0·01$ per cent. provided that the actual conductance data are of this order of precision and extend to $c = 0·00002$.

The conductivity data for solutions of potassium chloride over the range $c = 0·00001$ to $c = 0·001$ show[39] that the quantity $ca^2/(1-a)$ has a constant value in the case of solutions for which $c < 0·0001$. This result is regarded as direct evidence in favour of the validity of the law of mass action in its application to the ionisation of potassium chloride at very low concentration. Arrhenius has previously expressed[40] the view that the measurements of Kohlrausch and Maltby on solutions of sodium chloride and sodium nitrate are such as to indicate that the ionisation is governed by the mass law at high dilutions, and the supposition that the law is generally applicable under such conditions is shared by Washburn,[41] who contends that the ionisation constant has the same value for all univalent salts of the strong acids and bases. This author also draws the conclusion that the values of $ca^2/(1-a)$ for different salts of the type $M^·X^/$ remain identical at concentrations that are appreciably greater than those for which the mass law holds, and that the identity persists up to concentrations that

[36] E. W. Washburn, *J. Amer. Chem. Soc.*, 1918, **40**, 106; *A.*, ii, 55.

[37] H. J. Weiland, *ibid.*, 131; *A.*, ii, 56.

[38] E. W. Washburn, *ibid.*, 122; *A.*, ii, 55.

[39] H. J. Weiland, *loc. cit.*

[40] *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1913, **2**, No. 42; *A.*, ii, 93; compare *Ann. Report*, 1914, 26.

[41] *J. Amer. Chem. Soc.*, 1918, **40**, 150; *A.*, ii, 56.

increase as the salts under comparison resemble each other more closely.

Apart from the evidence which has been brought forward in favour of the operation of the law of mass action at high dilutions, it has to be recognised that the law fails completely to account for the general behaviour of the strong electrolytes, more particularly in the region $c = 0.0001$ to $c = 0.01$, where the actual observations are not seriously affected by correction factors, and as yet no satisfactory explanation of the so-called anomaly has been put forward. According to S. R. Milner,[42] the failure is so complete that insuperable difficulties stand in the way of any theory which attributes the variation of the conductivity with concentration to changes in the number of the ions. In his opinion, the strong electrolytes are completely ionised, and there is no question of non-ionised molecules in the usually accepted sense, although pairs of oppositely charged ions which are temporarily in close proximity may behave in certain cases as if they were bound together. The observed decrease in the molecular conductivity with increasing concentration is attributed mainly to a reduction in the mobilities of the ions under the influence of the interionic forces. The theoretical investigation [43] of this influence leads to the conclusion that a change in the concentration will produce identical variations in the conductivity and in the osmotic pressure of the ions. The effect of the interionic forces is to increase the frequency with which the ions are apparently associated, resulting in a reduction of the osmotic pressure of the ions. In consequence of the reduction of the time during which the ions are really free, the average mobility of the ions is diminished in the same ratio, and the experimental facts relating to the osmotic pressure and electrical conductivity of electrolytes can thus be accounted for.

The abnormality of strong electrolytes is further discussed in a series of papers by J. C. Ghosh, who is also of the opinion that the fundamental idea underlying the Arrhenius theory is not applicable to strong electrolytes. According to the theory which is alternatively suggested,[44] the relations between the ions are controlled by the electrical forces, and the interior of the electrolyte solution is characterised by a certain potential, A, which affords a measure of the work required to remove the ions from the influence of their mutual forces. Kinetic considerations suggest that the ions become "free" when their velocity exceeds a certain critical value, the fraction of the ions in this condition at any

[42] *Phil. Mag.*, 1918, [vi], **35**, 214 ; *A.*, ii, 54.

[43] S. R. Milner, *ibid.*, [vii], **35**, 352 ; *A.*, ii, 148.

[44] *T.*, 1918, **113**, 449.

moment being given by the expression $\alpha = e^{-A/nRT}$, in which n represents the number of ions formed from a molecule of the electrolyte. The actual number of "free" ions is $nNe^{-A/nRT}$, where N is the Avogadro number. Since at infinite dilution $A = 0$, it follows that

$$\frac{nN}{nNe^{-A/nRt}} = \frac{\Lambda_\infty}{\Lambda}$$

whence

$$\log \Lambda_\infty / \Lambda = \log 1/\alpha = A/nRT \quad . \quad . \quad . \quad . \quad (1)$$

In order to obtain the value of A, it is assumed that the marshalling of the ions in solution corresponds with the arrangement of the atoms in the crystallised electrolyte, and that the component ions form a completely saturated doublet. In the case of a binary electrolyte, these assumptions lead to the relation

$$A = E^2/Dr = E^2/D \sqrt[3]{r/2N} \quad . \quad . \quad . \quad . \quad (2)$$

in which E represents the ionic charge, D the dielectric constant of the medium, and r the distance by which the ions are separated. By the introduction of the Clausius virial theorem, the author's equations give for the connexion between the osmotic ratio i and the activity coefficient α the relation

$$i = n\{1 - \tfrac{1}{3} \log 1/\alpha\} \quad\quad\quad\quad (3)$$

It is claimed that the theory outlined affords a satisfactory account of the variation of the conductivity of salts with the concentration both in aqueous and in non-aqueous [45] solutions, and that the influence of temperature on the conductivity can be adequately explained by the change in the dielectric constant of the solvent, the effect of which can be calculated from equations (1) and (2). When, for binary and ternary salts, the values of the osmotic ratio i, obtained from freezing-point measurements, are compared [46] with the values calculated from equation (3) and also from the Arrhenius equation $i = 1 + (n-1)\alpha$, it appears that the former values agree more closely with experiment than the latter. The inferiority of the Arrhenius equation is particularly marked in the case of ternary electrolytes. Furthermore, it may be noted that the above equations lead directly to the empirical rule formulated by Walden on the basis of his investigations of the electrical conductance of his "normal electrolyte" in different solvents, according to which the value of the product $D \sqrt[3]{v}$ is independent the nature of the solvent if v represents the dilution corresponding with a fixed value of α.

The experimental values of α for the strong acids and bases are

greater than those calculated from the author's equations, and the anomaly is said to be directly connected with the high mobilities of the hydrogen and hydroxyl ions,[17] which are supposed to contribute to the conduction in a dual capacity. When the measured conductivities are corrected for the supplementary conduction effect, the strong acids and bases fall into line with the salts.

It is, of course, improbable that all the assumptions involved in the above theory will prove to be acceptable, but this notwithstanding, the reporter is of the opinion that the hypotheses present features, other than those of novelty, which entitle the theory to receive serious consideration.

Nature of Ions.

The frequently expressed opinion that ionisation is preceded by, and is, indeed, a consequence of combination between solute and solvent, has been further elaborated[48] and supported by evidence relating to the formation of hydrates by acids and bases. A review[49] of the known hydrates shows that isolable compounds are only formed by the stronger acids and bases. Furthermore, freezing-point measurements of solutions of acids of widely varying acid strength lend support to the view that the degree of hydration in aqueous solution increases with the strength of the acid as measured by its tendency to ionise.

According to the well-known formula of Stokes, the rate at which ions move in a particular medium under the influence of a given electric field is determined by the potential of the ionic charge. Smoluchowski, who considers that the transport of ions is to be regarded as the limiting case of cataphoresis, in which the inner and outer layers of the electrical "double layer" are widely separated in comparison with the radius of the ion, has derived the expression $u = KV/4\pi\eta$ for the mobility u, K being the dielectric constant of the medium, V the potential of the charged carrier, and η the viscosity of the medium. The only difference between this equation and that of Stokes lies in the numerical constant involved.

The fact that the mobilities of ions and of dispersoid particles are of the same order of magnitude would seem to indicate that the potential of the electric charge has approximately the same

[47] T., 1918, **113**, 790.

[48] J. Kendall and J. E. Booge, J. Amer. Chem. Soc., 1917, **39**, 2323 ; A., ii, 37.

[49] J. Kendall, J. E. Booge, and J. C. Andrews, ibid., 2303 ; A., ii, 36.

value in the two cases, and, according to G. von Hevesy,[50] the constancy of the mobility is to be regarded as evidence of a tendency on the part of the suspended charged particles, whether ionic or dispersoidal, to combine with the solvent until the potential reaches the approximate value of 70 millivolts. Assuming that the potential of the charged particle is given by $V = \epsilon/KR$, in which ϵ is the charge and R the radius of the particle, it is possible to calculate the radius of a normal univalent ion. Putting $\epsilon = 4.7 \times 10^{-10}$, $K = 81$, and $V = 0.07/300$, $R = 2.8 \times 10^{-8}$ cm. is obtained. For a normal multivalent ion, the radius will be directly proportional to the valency.

Expressed in terms of the ordinary units, the mobility of the normal univalent ion is 48, from which it may be inferred that univalent ions have little tendency to combine with water. Slowly moving ions of large size, such as the complex organic ions, are in a certain sense to be regarded as abnormal, in that the potential of the anhydrous ion is already less than that which tends to be set up by interaction with the solvent. Such ions do not therefore combine with water.

In support of the theory that the ratio ϵ/R has a constant value for the ionic carriers in a given medium, attention is directed to the fact that the rates of diffusion of the ions, which, theoretically, would be expected to depend mainly on the respective radii, bear a simple relation to the valencies of the ions. The available data for uni-, bi-, ter-, and quadri-valent ions give, indeed, average values for the reciprocals of the diffusion constants which are in the ratio $1 : 1.99 : 3.03 : 3.88$.

In applying the above considerations to the cataphoresis of relatively large aggregates (colloidal particles, gas bubbles), it should be noted that the potential of the charge is given by the equation $V = \epsilon(R_2 - R_1)/KR_1R_2$, in which R_1 is the radius of the particle and R_2 the thickness of the electrical double layer, which has been found[51] to be about 5×10^{-7} cm. Bearing in mind the approximate constancy of the potential, it follows that although the charge carried will be approximately proportional to the radius in the case of very small colloidal particles, it will increase with the size of the particles much more rapidly than the radius.

[50] *Kolloid Zeitsch.*, 1917, **21**, 129 ; *A.*, ii, 51.
[51] J. Stock, *Krakauer Anz.*, 1913, 131 ; 1914, 95. Compare also Smoluchowski in Graetz's " Handbuch der Elektrizität," **2**, 398.

Osmotic Pressure.

The contributions made to a recent general discussion of the subject of osmotic pressure, organised by the Faraday Society, convey the impression that the work which has been done during the last ten years on the experimental as well as on the theoretical side has not led to any generally accepted interpretation of osmotic phenomena in terms of the molecular theory. The diversity of views relative to the nature of osmotic pressure is, indeed, still so wide that there appears to be no real agreement on the question of whether so-called osmotic pressure is the cause of osmosis or the effect produced thereby. By some, the phenomena of osmosis are attributed to the activity of the molecules of the solute; by others, the molecules of the solvent are regarded as the important entities, and yet, again, a third view maintains that the interaction between molecules of solute and solvent is the prime factor to be considered.

According to A. W. Porter,[52] the theory which attributes the osmotic pressure to the molecules of the solute is the only theory yet advanced which reproduces the values of the osmotic pressure which have been actually obtained in experimental work. The osmotic pressure on this view represents the dynamical effect of the thermal motion of the solute molecules, and it may be supposed that the pressure resulting from the bombardment of the surface is an outwardly directed pressure which diminishes the Laplacian pressure by an equivalent amount. The author contends that arguments advanced against this theory, which are based on the difference in density, have been greatly weakened as a result of recent observations on Brownian motion.

What may be described as a highly specialised type of "vapour pressure" theory is advanced by W. R. Bousfield,[53] who rejects the idea that the molecules of the solute are directly responsible for the osmotic pressure. This theory involves the view that water consists of a mixture of three kinds of molecules—vapour or steam molecules (H_2O), liquid molecules (H_2O)$_2$, and ice molecules (H_2O)$_3$—and osmotic pressure is supposed to have its origin in the thermal agitation of the "steam" molecules. When a solute is added to water, there is supposed to be a reduction in the proportion of both the "steam" and "ice" molecules, resulting in a diminution of the vapour pressure and a lowering of the freezing point. The theory thus offers a plausible interpretation of certain

[52] *Trans. Faraday Soc.*, 1917, **13**, 123; *A.*, ii, 64.
[53] *Ibid.*, 141; *A.*, ii, 64.

well-known facts, but it can scarcely be said to possess the attributes required in an acceptable theory of osmotic pressure.

In the opinion of F. Tinker,[54] the pressure produced by the bombardment of the surface of the solution by the molecules of the solute is not to be confused with the osmotic pressure of the solution. The mechanism involved in an osmotic system consisting of solvent and solution separated by a semi-permeable membrane is such that no pressure is exerted on the membrane unless the osmotic tendency is counterbalanced. The resulting pressure is then exerted by the solution as a whole. The similarity between a dilute solution and a gas is entirely due to the circumstance that neither experiences a change in energy when the volume is changed, but equality in this respect is no criterion of identity of mechanism.

By applying the equipartition theorem to a two-phase system consisting of the solution of a volatile solute in contact with its vapour, J. R. Partington[55] has shown that the pressures due to the bombardment of the molecules of the solute on imaginary planes in the vapour and liquid phases must be equal if the concentration of the solute in the two phases is the same, for the equality of the average kinetic energies of the molecules of the solute in the two parts of the system has been definitely established by Perrin's experiments. There are said to be good reasons for the identification of this bombardment pressure with what is usually spoken of as the osmotic pressure of the solution.

Apropos of these divergent views relative to the molecular mechanism which gives rise to osmotic pressure, it may not be out of place to suggest that the actual facts for which an explanation is required should be kept clearly in view. The manifestation of osmotic pressure is limited to osmotic systems, and, so far as the isolated solution is concerned, osmotic pressure is a hypothetical quantity. The fact that there is no direct evidence of such pressure in an isolated solution does not, of course, detract in any way from its value as an eminently useful concept in the treatment of the problem of solution, but in so far as we are concerned with the interpretation of demonstrable facts, our attention must necessarily be mainly directed to the dynamics of osmosis and to the equilibrium conditions which are set up when the forces inherent in osmotic systems are counterbalanced by external forces.

Experiments made to ascertain whether osmotic effects are exhibited under conditions which seem to preclude the possibility of chemical reaction between the membrane and the solvent have

[54] *Trans. Faraday Soc.*, 1917, **13**, 133 ; *A.*, ii, 63.
[55] *Ibid.*, 194.

given results [56] which are positive in kind, although quantitatively the effects are very small in comparison with those which are obtained by the use of a copper ferrocyanide membrane. The chemically inert membranes were made by the compression of finely divided substances, such as copper, silver, gold, amorphous carbon, graphite, and silica, into disks, and the results obtained with these show that the magnitude of the osmotic effect increases as the diameter of the pores in the membranes decreases.

The data obtained for the osmotic pressure of sucrose solutions have been re-examined, [57] and it is pointed out that these are in satisfactory agreement with the equation $P(v-b)=RT$, where b is a constant which is greater than the volume of the contained sucrose. Assuming this to be due to the hydration of the sucrose molecules, the data for 20° give 5·3 as the average number of molecules of water associated with a molecule of sucrose.

Chemical Dynamics.

General velocity curves applicable to all complete reactions which belong to the same type have been drawn by G. W. Todd. [58] The nature of the curves may be illustrated by reference to a bimolecular reaction taking place at constant volume according to the equation $dx/dt=k(a-x)(b-x)$. If $x/a=X$, $ka=K$, and $b/a=p$, this equation assumes the form $dX/dt=K(1-X)(p-X)$, and on integration gives $Kt=\dfrac{1}{1-p}\log p(1-X)/(p-X)$.

By plotting X against Kt for different values of p, a series of curves is obtained which may be applied in practice for the determination of the velocity-coefficient k and of the value of X corresponding with any given time interval. The order of a reaction may also be ascertained by reference to the groups of curves which correspond with the different reaction types. Curves applicable to gas reactions proceeding to completion at constant pressure are also recorded. [59]

Some new observations [60] relative to the mode of action of the enzyme sucrase afford confirmation of the view that the inversion of sucrose is preceded by the formation of a compound between the sugar and the enzyme. When the latter is present in excess, the progress of the reaction from the beginning is that required

[56] S. L. Bigelow and C. S. Robinson, *J. Physical Chem.*, 1918, **22**, 99, 153; *A.*, ii, 156, 187.   [57] A. W. Porter, *loc. cit.*

[58] *Phil. Mag.*, 1918, [vi], **35**, 281; *A.*, ii, 102.

[59] *Ibid.*, 435; *A.*, ii, 190.

[60] H. Colin and Mlle. A. Chaudun, *Compt. rend.*, 1918, **167**, 338; *A.*, ii, 357.

by the equation for a unimolecular reaction, but with sucrose in excess the reaction proceeds with constant speed in the initial

Measurements of the velocity with which various micro-organisms are destroyed under the influence of dilute solutions of bactericidal agents show [61] that disinfection is an orderly time process which dynamically bears a close resemblance to purely chemical changes. The logarithmic nature of the process points to a far-reaching similarity of the individuals in a pure culture rather than to the dissimilarity which is postulated in the various theories of graded resistance by the supporters of the vitalistic view. It must be supposed that the resistance of the micro-organisms does vary, but the variation must be such that the number which are in a condition to be attacked at a given moment represents a constant proportion of the surviving micro-organisms. The supposed analogy between the process of disinfection and ordinary chemical changes is not in any way inconsistent with the specificity of disinfectants.

The selective influence of catalysts in fractional combustion processes and the poisoning of catalysts by the adsorption of reaction products are discussed in a series of papers [62] on the subject of contact catalysis, in which a number of new points are brought forward. In particular, it is suggested that cases of false equilibria may be due to the adsorption of the products of reaction, the reaction being brought to a standstill at a point which will depend on the relative amount of the catalyst in the reaction zone.

Results obtained in the investigation of the rate of dissolution of zinc alloys in hydrochloric acid [63] show that small quantities of arsenic, cadmium, and lead have no appreciable influence on the rate of dissolution of the zinc. The results obtained with these alloys are not in agreement with earlier observations, but it is supposed that the positive effects previously obtained were due to the presence of traces of iron or copper in the alloys used. The facts brought to light by the new experiments would seem to be difficult to reconcile with the theory of local elements.

[61] R. E. Lee and C. A. Gilbert, *J. Physical Chem.*, 1918, **22**, 348; *A.*, ii, 262.

[62] W. D. Bancroft, *ibid.*, 1917, **21**, 644, 734; 1918, **22**, 22; *A.*, ii, 13, 40, 105.

[63] M. Centnerszwer, *Zeitsch. physikal. Chem.*, 1918, **92**, 563; *A.*, ii, 162.

Reaction Velocity and the Quantum Theory.

Work in this field has been continued[64] by W. C. M. Lewis. The fundamental assumption underlying the author's radiation hypothesis is that the active mass of a reacting substance depends not only on its concentration, but also on the density of the thermal radiation in the system which is of the type capable of being absorbed by the substance. Since the radiation and the matter are at the same temperature, Planck's quantum theory may be applied to the exchanges.

It has already been shown that the heat change accompanying a reaction and the influence of temperature on the velocity of reaction can be expressed in terms of the critical increment, defined as the energy required to bring an average molecule into the reactive condition, and an attempt is now made to calculate reaction velocities.

In this connexion, it is necessary to draw a clear distinction between unimolecular reactions and reactions of higher order. Reactions belonging to the latter group depend on encounters between activated molecules, and from a knowledge of the critical increment, which may be most conveniently derived from the observed temperature-coefficient of the reaction, it is shown to be possible to calculate the velocity-coefficients of bimolecular gaseous reactions. The values obtained in this way for the decomposition of hydrogen iodide and for the combination of hydrogen and iodine are in conformity with the data of Bodenstein and of Stegmüller.

In the case of unimolecular reactions, intermolecular transactions are of no account, the molecules undergoing spontaneous transformation in accordance with the law of probability. Activated molecules as defined by the critical increment are non-existent, and the kinetic theory affords no assistance in the calculation of the velocity-coefficient.

It is claimed, however, that such unimolecular coefficients can be calculated from an empirical expression, based on the radiation hypothesis, which has been applied to the dissociation of iodine, bromine, chlorine, and hydrogen. Since the critical increment of the free atoms of these elements corresponds with the infra-red region, and is therefore small, it may be assumed that the free atoms of these substances are all, or nearly all, in the active state. This assumption permits of the calculation of the velocities with which the atoms recombine to form molecules, and these in combination with the experimentally determined equilibrium constants

lead to values for the unimolecular coefficients which determine the
velocity of dissociation.   These "observed" values are satisfactorily
reproduced by the empirical expression referred to   The deriv-
ation of a rational expression for the simplest type of chemical
change on the basis of the radiation hypothesis can as yet only be
contemplated as a possibility.

Inflammability of Gas Mixtures

Observations on the inflammability of mixtures of methane and
air [65] show that the effect of increasing the initial temperature of
the mixtures is to widen the difference between the composition of
the upper and lower limiting mixtures   This result is quite in
accordance with theoretical predictions.   Increase in the pressure
has the effect of increasing the percentage of methane in both the
limiting mixtures.

In the course of these observations on the influence of tempera-
ture and pressure on inflammability, it has been found that the
lowest pressure at which self-propagation of flame occurs in
methane–air mixtures at the ordinary temperature is 120 mm.
The much higher value of 300 mm. previously recorded [66] is prob-
ably due to the deficient character of the means of ignition
employed in the earlier experiments.

Examination of the "uniform movement" in tubes of small
diameter filled with mixtures of methane and air has shown [67] that
the cooling effect of the walls, which increases as the diameter
diminishes, produces a considerable narrowing of the range of
mixtures which are inflammable.   In such tubes the speed of pro-
pagation tends towards a constant value (35 cm. per second) as the
upper and lower limits are approached, and this apparently is to
be regarded as the minimum speed at which the continued pro-
pagation of flame is possible.

The Inflammation Process

A study of the phenomena associated with the central ignition
of inflammable mixtures in closed spherical vessels has shown [68]
that the flame expands symmetrically if the speed is sufficiently
great.   On the other hand, if the speed of propagation is smaller,
the flame is propagated more quickly in the upward direction, with

[65] W. Mason and R. V. Wheeler, *T.*, 1918. **113**, 45.

[66] G. A. Burrell and I. W. Robertson, *U.S. Bureau of Mines*, 1916, No. 121.

[67] W. Payman and R. V. Wheeler, *T.*, 1918, **113**, 656.

[68] R. V. Wheeler, *ibid.*, 840.

the result that cooling, due to contact of the flame with the top of the explosion vessel, sets in before the whole of the inflammable gas is burnt.

The explosion vessels used in these experiments were fitted with a manometric device for recording the pressure changes during the inflammation process. Pressure–time curves constructed from the records show three distinct stages, in which the pressure increases regularly, remains constant, and then gradually decreases. The constant pressure stage is presumably connected with the equalisation of temperature differences, for when this is accelerated by fitting the explosion vessel with a rapidly revolving small fan, the constant pressure part of the curve disappears.[69]

Residual and Extinctive Atmospheres of Flames.

By comparing the amounts of oxygen in the atmospheres which are left behind when the flames of combustible gases, burnt in a limited supply of air, are extinguished, it has been found[70] that the oxygen content of the residual atmosphere depends mainly on the rate of diffusion of the combustible gas and on the complexity of the combustion process. The variations are considerable, as may be seen from the following numbers representing the percentage of oxygen: hydrogen 5·7, carbon monoxide 10·2, cyanogen 15·3, methane, ethane, propane between 15·6 and 16·4, the values increasing regularly with the molecular weight of the hydrocarbon.

Similar results were obtained in other experiments in which the flames were fed with mixtures of air and nitrogen, the relative quantities of which could be varied with considerable nicety. The extinctive atmospheres found for the first five members of the methane series show very nearly the same percentage of oxygen (16·3—16·6) when the gases are supplied at constant speed. If the speed of the air–nitrogen mixture is increased, the flames continue to burn, however, in atmospheres which would extinguish them if supplied at a lower speed.

Colloids.

In last year's Report,[71] attention was directed to observations on the structure of the thin films which are deposited on a glass surface when various elements are heated in a high vacuum.

[69] *Third Report of Explosions in Mines Committee*, 1913, p. 26.
[70] T. F. E. Rhead, *J. Soc. Chem. Ind.*, 1918, **37**, 274 ; *A.*, ii, 362.
[71] *Ann. Report*, 1917, 24.

Further experiments[72] have shown that the structure of such films depends on the melting point of the element, in that elements which melt at high temperatures give rise to films which are entirely, or for the most part, devoid of structure, whilst elements of lower melting point show a tendency to form deposits in which ultra-microns are clearly recognisable as structural units. When, however, the glass surface on which the metal vapours condense is cooled by means of liquid air, the films obtained from the metals of the second group resemble in many cases those given by metals of high melting point. The structureless films quickly assume a heterogeneous appearance when the temperature is raised.

Incidentally, it has been observed that the colour of the film is the same whether the condensate is structureless or ultramicroscopically heterogeneous. From this, it is inferred that the colour is due to the selective absorption of the atoms, and is therefore a characteristic property of the metal. The observation has a direct bearing on the general question of the connexion between the colour and degree of dispersity of colloidal systems. Although a considerable amount of apparently plausible evidence has been advanced in favour of such connexion, there are equally good grounds for the alternative view that colour variation in colloid systems has nothing to do with the fineness of the colloid structure. The same divergence is shown by recent expressions of opinion, for whereas it is argued, on the one hand,[73] that the colour relations exhibited by comparable series of disperse particles, whether atomic, ionic, or colloidal, are fundamentally related to the size of the particles, it is to be noted that the investigation[74] of the colour and ultramicroscopic appearance of various indicators in acid, neutral, and alkaline solution has furnished no evidence in support of the view that the colour changes are in any way related to the degree of dispersity of the indicators.

The anisotropy exhibited by certain colloidal solutions has been further examined,[75] and observations on vanadic acid sols, prepared under different conditions, show that there is no recognisable line of demarcation between the particles which are present in the freshly prepared isotropic sols and those which can be microscopically identified as crystalline particles present in colloidal solutions which have been kept for some time. In the freshly prepared sols, the ultra-microns are spherical, but on heating at 100°, elongated

[72] W. Reinders and L. Hamburger, *Proc. K. Akad. Wetensch. Amsterdam,* 1918, **20,** 1135 ; *A.,* ii, 312.

[73] F. Kirchhof, *Kolloid Zeitsch.,* 1918, **22,** 98 ; *A.,* ii, 300.

[74] H. R. Kruyt and I. M. Kolthoff, *ibid.,* 1917, **21,** 22 ; *A.,* 1917, ii, 452.

[75] W. Reinders, *ibid.,* 1917, **21,** 161 ; *A.,* ii, 101. Compare *Ann. Report,* 1916, 22.

ultra-microns make their appearance in a short time, and the sol becomes doubly refracting.

Brief reference may be made to some interesting observations [76] on the behaviour of telluric acid and its alkali salts, which indicate a remarkable tendency on the part of these substances to undergo polymerisation with the formation of aggregates, which in their influence on the freezing point, boiling point, and electrical conductivity of the solution exhibit the character of colloids (semicolloids). The lithium, sodium, and potassium salts have, moreover, no definite solubility in water; the quantity of water in the crystals varies with the concentration of the solutions from which they have been deposited, whilst the crystals undergo dehydration without any appreciable change in appearance. The substances in question not only adsorb water, but take up considerable quantities of alkali hydroxide and telluric acid, and on this account the statements made with respect to the alkali tellurates in the older literature must be accepted with reserve.

The measurement of the potential differences [77] which result from the flow of electrolytes through capillary glass tubes has shown that equivalent solutions of the chlorides of uni-, di-, and ter-valent metals give rise to effects which depend on the valency of the cation. The relations are substantially the same as those brought to light in the investigation of the influence of the chlorides of potassium, barium, and aluminium on the stability of hydrocarbon oil emulsions,[78] and both effects are presumably due to surface adsorption of the electrolytes. The potential measurements afford evidence that very dilute solutions do not reduce, but raise the contact potential, and this fact is apparently connected with the well-known peptonising influence of such dilute solutions and has an obvious bearing on the view held by certain colloid chemists that minute traces of electrolytes are essential for the stability of colloidal solutions.

An improved form of electro-osmometer,[79] with which various electro-endosmotic phenomena have been carefully investigated, calls for a passing note. Results obtained with this instrument in the examination of dilute acid and alkaline solutions confirm Perrin's observation relative to the existence of an isoelectric point.

[76] A. Rosenheim and G. Jander, *Kolloid Zeitsch.*, 1918, **22**, 23 ; *A.*, ii, 194.

[77] H. R. Kruyt, *ibid.*, 81 ; *A.*, ii, 289.

[78] Compare *Ann. Report*, 1915, 14.

[79] T. R. Briggs, H. S. Bennett, and H. L. Pierson, *J. Physical Chem.*, 1918, **22**, 256 ; *A.*, ii, 214.

Miscellaneous.

Brief reference may be made, finally, to a number of papers of miscellaneous character.

F. M. Jaeger[80] has summarised the results of his extensive investigations on the surface energy of liquids, the results for some 200 organic liquids and 50 inorganic compounds over a wide range of temperature being compared. The curves which are obtained by plotting molecular surface energy against temperature are not, for the most part, straight lines, and it follows that Eötvös's rule is not generally applicable, and also that the specific heat of the surface layer must be different from that of the liquid in bulk.

Improvements[81] have been made in the technique of the measurement of contact potentials and in methods of producing definite differences of potential at liquid-liquid surfaces.

With the view of procuring data required in the calculation of the free energy of formation of important classes of compounds, the conditions of equilibrium in various reversible reaction systems have been examined.[82] This forms part of a comprehensive scheme of research which is being undertaken by American chemists.

In a contribution to the question of the structure of solids, A. H. Compton[83] brings forward a number of new arguments in support of the view that in the solid state of aggregation the atoms are so intimately intermingled that particular molecules cannot be said to have any real existence.

The further investigation of the constitution of aqueous soap solutions by measurement[84] of the rate at which nitrosotriacetonamine is decomposed with the liberation of nitrogen under the influence of the hydroxyl ion, has given results for the alkalinity which are in substantial agreement with those previously obtained by the potential method. The alkalinity of the solutions is so small as to preclude the possibility of the existence of any considerable amount of free fatty acid in the solutions. Free fatty acid

[80] *Zeitsch. anorg. Chem.*, 1917, **101**, 1; *A.*, ii, 33.

[81] G. N. Lewis, T. B. Brighton, and R. L. Sebastian, *J. Amer. Chem. Soc.*, 1917, **39**, 2245; *A.*, ii, 25.

[82] Compare G. N. Lewis and D. B. Keyes, *ibid.*, 1918, **40**, 472; *A.*, ii, 153; G. N. Lewis and T. B. Brighton, *ibid.*, 482; *A.*, ii, 153; M. Randall and F. R. von Bichowsky, *ibid.*, 368; *A.*, ii, 159.

[83] *J. Franklin Inst.*, 1918, **185**, 745; *A.*, ii, 300.

[84] J. W. McBain and T. R. Bolam, *T.*, 1918, **113**, 825.

added to the solution is adsorbed or combined with the formation of acid soaps.

Although the soaps in aqueous solution behave as colloidal electrolytes in which the normal anions are replaced by highly charged aggregates or micelles, the physical properties of alcoholic solutions indicate[85] that both the soaps and the free fatty acids behave as normal electrolytes when dissolved in ethyl alcohol.

H. M. DAWSON.

[85] Miss M. E. Laing, *T.*, 1918, 113, 435.

INORGANIC CHEMISTRY.

The diminution in the number of papers that come under review in this branch is very marked. With few exceptions, the work in inorganic chemistry during 1918 has been restricted to the preparation of new substances. There is little to record of outstanding interest beyond the preparation of the hydrides of silicon and some of their halogen and oxygen derivatives.

Allotropy.

Some further work on the allotropy of sulphur may be referred to.[1] The discovery of the third modification of sulphur, namely, S_π, was dealt with in the Report for 1913, the method of preparation being to heat sulphur at 170° and then to cool it rapidly. The sulphur is then dissolved in carbon disulphide and cooled to −80°, when the whole of the S_λ separates out, leaving the S_π in solution. By careful evaporation of this solution in a vacuum at −80°, the S_π is obtained, contaminated with only a very small quantity of S_μ. It is clear, therefore, that S_π is formed from S_λ at 170°. It has now been found that the equilibrium between the two forms is obtained more rapidly in sulphur chloride solution than in toluene. At 140°, six hours are required in the case of toluene, whereas equilibrium is reached in a few minutes in sulphur chloride solution. Some quantitative investigations have been made of the amount of S_π formed under varying conditions of temperature and concentration. Solutions of sulphur in toluene, in which the equilibrium between S_λ and S_π had been established by heating at 140°, 150°, and 160°, were cooled to 0° and stirred for an hour in contact with rhombic sulphur. The resulting solutions were analysed, and it was found that the proportion of S_π increases with the temperature and also slightly with the concentration.

There is no doubt that the discovery of this new form of sulphur

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[1] A. H. W. Aten, *Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 824 ; *A.*, ii, 193.

which is clearly produced from S_λ at temperatures above the melting point must alter our ideas as to the composition of molten sulphur. For example, it has commonly been believed that the natural freezing point of sulphur is lower than that of pure rhombic sulphur, S_λ, owing to the presence of about 3·7 per cent. of amorphous sulphur, S_μ.[2] Since S_λ is partly converted into S_π, it is evident that the latter must be present in sulphur at its melting point, and the question at once arises as to how far the natural freezing point of sulphur is due to the presence of S_π. This question has been very definitely answered, for it has been found that S_π is the sole factor in depressing the freezing point of S_λ.[3, 4]

It was necessary in the first place to determine the cryoscopic constant of sulphur, and this was carried out without much difficulty, since sulphur can be used as a cryoscopic solvent if certain conditions are fulfilled. Soon after it has been melted, the freezing point of sulphur is about 119°, but after it has been kept for some hours at a temperature just above its melting point, the freezing point falls to the natural freezing point, 114·5°. In this condition, the sulphur is suitable for cryoscopic determinations. The cryoscopic constant was determined by means of a number of organic compounds, the mean value being 213. The actual determinations were: bromoform 229·3, phenylthiocarbimide 226·6, naphthalene 211·4, diphenyl 208·4, thymol 206·4, quinoline 205·7, β-naphthol 205·2, and aniline 201·8.

Now the freezing point of S_λ is 119·25°, whilst the natural freezing point is 114·5°. Assuming that the depression of 4·75° is due to the presence of S_π with a molecular weight of 128, the proportion of S_π present must be 2·78 per cent. In order to test whether this assumption is justified, some experiments were made on the effect of the addition of various forms of sulphur to sulphur of freezing point 114·5°. Amorphous sulphur, S_μ, prepared in a variety of ways, has practically no effect on the freezing point, and this is due to the rapid transformation of the S_μ to a mixture of S_λ and S_π of the same composition as the solvent sulphur. If the solution is rapidly cooled after the addition of the S_μ, it is found that only about 24 per cent. of the added sulphur is still insoluble in carbon disulphide, the remainder having been transformed into S_λ and S_π. When S_μ is added to a fused mass having a lower

² A. Smith and C. M. Carson, *Proc. Roy. Soc. Edin.*, 1906, **26**, 352; *A.*, 1907, ii, 20.

³ E. Beckmann and C. Platzmann, *Zeitsch. anorg. Chem.*, 1918, **102**, 201; *A.*, ii, 218.

⁴ E. Beckmann, R. Paul, and O. Liesche, *ibid.*, 1918, **103**, 189; *A.*, ii, 308.

freezing point than 114·5°, there is no effect, but if it is added to one having a higher freezing point than 114·5°, it has the effect of lowering it towards the natural freezing point. indicating that at the higher temperature relatively more S_π is formed from the S_μ.

When S_μ is heated, it shows no sharp melting point, but, having reached 120°, it has at once the natural freezing point 114·5°. If a mixture of rhombic sulphur with about 5 per cent. of S_μ is melted, it has a freezing point about 2° lower than that of rhombic sulphur, indicating that under these conditions the S_λ decomposes into 23 per cent. S_π and 77 per cent. S_λ. A sample of S_π when added to sulphur with the natural freezing point lowered the freezing point slightly, but the depression indicated only about 4·6 per cent. S_π in the sample. Lastly, it was observed that both rhombic and monoclinic sulphur raised the natural freezing point of sulphur by increasing the proportion of S_λ.

It may not be out of place to direct attention here to the remarkable colour gradation exhibited by the various allotropic modifications of sulphur in solution. It has now been definitely recognised that there are four distinct modifications, namely, S_λ, S_μ, S_π, and S_ϕ, and of these S_λ is known as the ordinary rhombic and monoclinic varieties. When S_λ is maintained at temperatures of 119—170°, it is partly transformed into S_π, the molten mass being an equilibrium mixture of S_λ and S_π, the proportion of S_π being increased with rise of temperature. At temperatures of 250—300°, S_μ is formed, for it is a simple matter to prove by sudden cooling that a considerable proportion is insoluble in carbon disulphide. Clearly, therefore, S_π and S_μ are formed by the supply of energy to S_λ, and although both are known in the solid state, they obviously are metastable. This is proved by the readiness with which S_μ is converted into S_λ and S_π by solution in molten sulphur maintained at 120°, as described above.

S_ϕ is precipitated along with S_μ when certain sulphur compounds, such as sodium thiosulphate, are treated with mineral acid, and from this alone the relative energy contents of S_ϕ and S_λ cannot be ascertained.

Now it is well known that a solution of S_λ in carbon disulphide is practically colourless, and, further, a solution of S_π in toluene has a colour analogous to that of a concentrated solution of potassium chromate. It is not generally known that S_μ is soluble in piperidine, and the solution has a fine red colour analogous to the colour of molten sulphur at a temperature of 250—300°. Since molten sulphur at 250—300° contains S_μ as an important constituent of the equilibrium, this identity of colour is not sur-

prising. Again, S_λ is soluble in piperidine, and the solution has the same colour as when S_μ is dissolved in that solvent, and thus it is evident that piperidine converts S_λ into S_μ. Further on neutralising the piperidine solution with acid, the dissolved sulphur is recovered as S_μ.

We have, therefore, three differently coloured solutions of sulphur, namely, the almost colourless solution of S_λ in carbon disulphide, the strongly yellow solution of S_π in toluene, and the deep red solution of S_μ in piperidine. This deepening of the colour, coupled with the knowledge that the energy content increases from S_λ to S_π to S_μ, is very suggestive. It is exactly analogous to the cases of many organic compounds which exhibit different colours in different solvents, according to the amount of energy supplied to them by the solvents. According to this argument, S_ϕ must have an energy content between those of S_λ and S_π, since its solutions exhibit a colour intermediate between those of the solutions of these two.

The colour of the various phases of sulphur would seem to have a bearing on the constitution of the sulphides and the polysulphides. The anhydrous monosulphides of the alkali metals are practically white, the disulphides pale yellow, the tetrasulphides deep yellow, and the pentasulphides orange. In short, the colours are analogous to those of the four modifications or phases of sulphur when in solution. The suggestion may at once be made that the phases in which the sulphur exists in the four types of sulphides corresponds with the four phases of sulphur, S_λ, S_ϕ, S_π, and S_μ. Considerable support for this is to be found in the fact that the pentasulphides, on treatment with acids, give a precipitate of S_μ.

Colloids.

Amongst the papers on colloids that have been published during the last twelve months, a few have described the preparation of inorganic colloids.

Colloidal solutions of nickel can be prepared by the reduction of solutions or suspensions of nickel salts in glycerol containing gelatin or gum arabic as a protective colloid.[5] Thus, a solution of nickel formate and gelatin in glycerol at 200—210° when submitted to the action of a stream of hydrogen assumes a chestnut-brown colour. The colloidal solution remains unaltered in air and is miscible with alcohol. On treatment with water and centrifuging, the colloidal metal is deposited as a brown solid containing 25 to 30 per cent. of nickel. This again yields colloidal

[5] C. Kelber, *Ber.*, 1917, **50**, 1509 ; *A.*, ii, 19.

nickel solutions in dilute acetic acid, acidified water, glycerol, or alcohol.

Hydrazine hydrate, formaldehyde, hydroxylamine, and hypophosphorous acid can be used as reducing agent, and the nickel formate can be replaced by nickel acetate or freshly precipitated nickel hydroxide.

A variety of methods have been described for the preparation of mercury sols,[6] and the methods may be grouped into three classes, namely, mechanical, thermal, and electrical dispersion. By forcing a fine stream of mercury by means of high pressure into solutions of gelatin and potassium nitrate, definite mercury sols are produced, although the particles are relatively large. When mercury is shaken with very dilute solutions ($10^{-5}N$) of ammonia, ammonium sulphate, ammonium chloride, calcium citrate, tartaric acid, potassium tartrate, carbamide, or gelatin, colloidal mercury solutions are produced.

Mercury sols are also formed by passing hot mercury vapour directly into water. They can also be prepared by the Bredig method, using either a direct or an alternating current.

The sols have varying colours from grey to yellowish-brown and reddish-brown. They are all positively charged except those prepared in citrate or tartrate solutions, which are negatively charged.

Reference may also be made to an important investigation of the nature and stability of hydrated ferric oxide sols.[7] Several series of perfectly clear sols were prepared, the iron concentration in each being constant, whilst the chlorine content varied. The sols were prepared by oxidising a solution of ferrous chloride containing 1 gram equivalent in 400 c.c. of solution by means of 3 per cent. hydrogen peroxide. The solutions were then dialysed and diluted to the required concentration.

The sols were precipitated by potassium sulphate solution, and the amount of salt required for the complete precipitation of the sol was taken as a measure of its relative stability. The results show that for a given iron concentration the stability increases with the chlorine concentration, whilst for sols of a given purity, that is, for sols with the same ratio, Fe/Cl, the stability decreases as the concentration increases, this being most pronounced in very pure sols.

A theory based on the existence of definite oxychlorides as components of the colloid equilibrium was put forward by Nicolardot,[8]

[6] I. Nordlund, *Diss.*, Upsala, 1918, 1 ; *A.*, ii, 267.

[7] M. Neidle, *J. Amer. Chem. Soc.*, 1917, **39**, 2334 ; *A.*, ii, 45.

[8] P. Nicolardot, *Compt. rend.*, 1905, **140**, 310 ; *Ann. Chim. Phys.*, 1905, [viii], 6, 334 ; *A.*, 1905, ii, 167.

who believed that two such oxychlorides exist with ratios Fe : Cl of 6 and 125. The experimental data are now criticised and the theory is modified. The first stage in the hydrolysis of ferric chloride is to be represented by the equation

Ferric chloride + water $\rightleftharpoons$ colloid No. 1 + hydrochloric acid,

colloid No. 1 being an oxychloride in which the ratio, Fe/Cl, is 21. It is believed that all clear, hydrated ferric oxide sols containing ferric iron contain this definite oxychloride as a component of the equilibrium.

As the concentration of ferric ion is decreased, this colloidal oxychloride begins to hydrolyse, giving hydrochloric acid and a second oxychloride, colloid No. 2, with a ratio greater than 21. When the sol no longer contains ferric ion, the progressive removal of the hydrochloric acid causes a series of successive hydrolyses which overlap to a certain extent, and oxychlorides of increasing molecular weight are formed.

The hydrolysis equilibria of the oxychlorides are established rapidly, but the establishment of the first hydrolytic equilibrium between ferric chloride and colloid No. 1 requires considerable time.

Group I.

Some new investigations have been carried out on sodamide and potassamide.[9] These compounds were prepared by the action of ammonia on the molten metals, and their physical constants were determined immediately after preparation. The melting points were found from cooling curves to be $NaNH_2$ 210°, KNH_2 338°, these being much higher than those found by Titherley,[10] namely, $NaNH_2$ 149—155° and KNH_2 270—272°. No other breaks were found in the cooling curves. The fused amides conduct electrolytically owing to their ionisation into $Na^{\cdot}$ and $NH_2{}'$. Hydrazine, however, is not formed at the anode, but ammonia and nitrogen, owing probably to the action of the amide. Chlorine and iodine do not give hydrazine with these compounds, but halogen-substituted ammonias.

Certain mixed polyhaloid salts of ammonium and the alkali metals have been prepared.[11] It has been known for some time that by the action of bromine vapour on ammonium iodide, the bromoiodo-bromide, NH_4BrIBr, is formed.[12] Although at the

[9] L. Wöhler and F. Stang-Lund, *Zeitsch. Elektrochem.*, 1918, **24**, 261 ; *A.*, ii, 397.   [10] A. W. Titherley, *T.*, 1894, **65**, 504.
[11] W. N. Rae, *ibid.*, 1915, **107**, 1286 ; 1918, **113**, 880.
[12] C. L. Jackson and I. H. Derry, *Amer. Chem. J.*, 1900, **24**, 15 ; *A.*, 1900, ii, 596.

commencement of the reaction iodine is set free, this substance is not a mixture of ammonium bromide and iodine bromide, but a definite compound. Exactly analogous compounds are formed by the slow action of bromine vapour on potassium, rubidium, and cæsium iodides These substances are ruby-red in colour and deepen in shade with rise in atomic weight of the metal. When heated, they lose iodine monobromide and give the normal bromide.

By the action of chlorine [13] on concentrated solutions of the iodides of the alkali metals, the compounds $MICl_4$ have already been prepared, and two of these salts have water of crystallisation, namely, $LiICl_4,4H_2O$ and $NaICl_4,2H_2O$. By the action of dry chlorine on the dry iodides, these salts have been prepared in the anhydrous condition, their colour varying from deep orange in the case of the lithium salt to mustard-yellow in the case of the cæsium salt. The lithium salt, however, could not be obtained in the anhydrous condition, and the hydrate, $LiICl_4,3H_2O$, was prepared. Although the rate of absorption of the chlorine falls off as the formation of the pentahaloid approaches completion, the time curve shows no break. On the other hand, when these salts are gently heated, they lose chlorine and are converted into the trihaloid salts, $MICl_2$. The latter compounds are much more stable than the pentahaloid salts and require to be heated at a higher temperature in order to give the normal chloride with loss of iodine monochloride.

Mention may be made of an extension of the work that has previously been reported on the sulphides of sodium and potassium.[14] The investigation has now been carried to the polysulphides of these two metals, two experimental methods having been adopted. In one, the rate was measured at which sodium tetrasulphide and potassium pentasulphide lose sulphur when heated in a steady stream of hydrogen, and in the other the freezing-point curves for the systems Na_2S–S and K_2S–S were determined. The results obtained are of some interest, for definite evidence was forthcoming of the existence of a complete series of compounds of the general formula R_2S_x, where x is a whole number and has the maximum value 5 in the sodium series and 6 in the potassium series. No evidence whatever was found of the existence of any intermediate compounds, such as the enneasulphide, Na_4S_9, described by Bloxam. In connexion with the desulphurisation of the polysulphides, the disulphides were found to be extremely stable compounds from which sulphur can only be removed with difficulty at 700—800°.

[13] H. L. Wells and H. L. Wheeler, *Amer. J. Sci.*, 1892, [iii], **44**, 42 ; *A.*, 1893, ii, 68.   [14] J. S. Thomas and A. Rule, *T.*, 1917, **111**, 1063.

In order to decide between the simple formula R_2S, and the doubled formula, R_4S_{2x}, favoured by Bloxam, the molecular weights of sodium disulphide and tetrasulphide and potassium pentasulphide were determined by the ebullioscopic method with alcohol as a solvent. The results obtained were considerably lower even than those required by the simpler formulæ. The green colour of the solutions suggests that a certain amount of alcoholysis occurs, but as very little hydrogen sulphide is lost by the boiling solution, it is probable that the discrepancy is not due to this cause. In all probability, the explanation is to be found in ionisation having occurred, and at any rate it is evident that the simpler formula, R_2S_x, must be correct.

The relative stability of the disulphides at once suggests that their constitution is to be represented by $R \cdot S \cdot S \cdot R$. From this, the polysulphides are obtained, not by solution of sulphur, but by

further combination to $R \cdot \overset{S}{\underset{}{S}} \cdot S \cdot R$ and $R \cdot \overset{S}{S} \cdot \overset{S}{S} \cdot R$.

It has been found that the commercial basic carbonates of copper differ very considerably in composition, and it is erroneous to assume that they approximate to the composition of malachite.[15] An analysis of thirteen samples from different commercial sources showed that the percentage of copper oxide varied from 78·6 to 66·2, and from this point of view it would seem that the composition more nearly approximates to that of azurite. The amount of carbon dioxide present, on the other hand, is much below that required for either malachite or azurite. Some attempts to prepare a basic carbonate of copper of approximately constant composition by mixing solutions of copper sulphate and sodium carbonate or sodium hydrogen carbonate led to negative results. It has been found, however, that a definite basic salt is obtained in the following way. A solution of copper sulphate, saturated at 14·5°, is diluted with an equal volume of water, and to this solution is added a solution containing 5 per cent. of sodium carbonate and 5 per cent. of sodium hydrogen carbonate until precipitation is complete. The mixture is allowed to remain for twelve hours and then filtered. The precipitate is washed free from sulphate, a process which takes many hours. The wet precipitate is allowed to remain for another twelve hours, and then is dried in a steam-oven for at least six hours. The formula of the salt prepared in this way is $2CuCO_3, 5Cu(OH)_2$ or $7CuO, 2CO_2, 5H_2O$.

[15] H. B. Dunnicliff and S. Lal, T., 1918, 113, 718.

Group II.

When solutions of magnesium chloride and disodium, dipotassium, or dirubidium hydrogen phosphate are brought together, magnesium hydrogen phosphate generally is precipitated. This salt has a variable content of water of crystallisation, but is liable to be contaminated with magnesium monoalkali phosphate, and under suitable conditions the whole of the precipitate may consist of the latter type of salt.[16] For example, when a dilute solution of magnesium chloride is added slowly with agitation to a 10 per cent. solution of dipotassium hydrogen phosphate, the salt, $MgKPO_4,6H_2O$, is precipitated in almost pure condition. The corresponding rubidium salt can be precipitated almost pure in a similar manner. If the two solutions are mixed in the reverse order, the precipitate obtained is of uncertain composition, containing various quantities of $MgKPO_4$, $MgHPO_4$, $Mg(OH)_2$, and $Mg_3(PO_4)_2$. In whatever manner dilute solutions of magnesium chloride and disodium hydrogen phosphate are mixed, there is a danger of the magnesium hydrogen phosphate being contaminated with magnesium alkali phosphate. This has a bearing on the estimation of phosphoric acid by the magnesium method, since it is desirable to guard against the presence of alkali metal salts.

Calcium hydrogen arsenate can be prepared by pouring a solution of calcium chloride, slightly acidified with acetic acid, hydrochloric acid, or nitric acid, into a solution of disodium hydrogen arsenate similarly acidified.[17] The precipitate is washed by decantation, filtered, washed until free from chlorides, and dried at 100°. The composition of the salt is $CaHAsO_4,H_2O$, the water of crystallisation being lost at 175°.

By the addition of an alkaline solution of calcium chloride to an alkaline solution of disodium hydrogen arsenate, pure calcium arsenate, $Ca_3(AsO_4)_2,2H_2O$, is obtained, which can be dried at 100°.

An important contribution to the literature on mercuriammonium compounds may be noted.[18] There are three classes of these substances, namely: (i) the additive compounds of mercuric salts and ammonia, of which fusible precipitate, $HgCl_2,2NH_3$, is the best known example; (ii) the ammonolysed compounds in which NH_2, NH, or N takes the place of the acid radicle in a mercuric salt, of which infusible precipitate, $ClHgNH_2$, is the simplest representative; (iii) the compounds

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[16] D. Balareff, *Zeitsch. anorg. Chem.*, 1918, **102**, 241 ; *A.*, ii, 266.

[17] R. H. Robinson, *J. Agric. Res.*, 1918, **13**, 281 ; *A.*, ii, 232.

[18] Miss M. C. C. Holmes, *T.*, 1918, **113**, 74.

which are both hydrolysed and ammonolysed, such as the chloride of Millon's base, $H_2N \cdot Hg \cdot O \cdot HgCl$.

By the action of gaseous ammonia on mercuric chloride, fusible precipitate is formed, and this compound can also be obtained by dissolving infusible precipitate or the chloride of Millon's base in a hot saturated solution of ammonium chloride and cooling the solution. Some experiments carried out on the action of dry ammonia on an ethereal solution of mercuric chloride indicated that a lower amine of mercuric chloride must exist. When infusible precipitate is digested at 100° with solutions of mercuric chloride in approximately saturated solutions of ammonium chloride, the solution being filtered while hot from the undissolved precipitate, the filtrate, on being allowed to cool, slowly deposits well-defined crystals. The composition of these crystals depends on the concentration of the mercuric chloride. When the latter amounts to 110 grams in 100 grams of water containing 42 grams of ammonium chloride, the new compound, $3HgCl_2,2NH_3$, is obtained. With smaller concentrations of mercuric chloride, fusible precipitate is formed, and no compounds intermediate between these two appear to exist.

Some doubt has been thrown on the existence of the compound, $HgCl_2,NH_2 \cdot HgCl$, but it is now found that this substance is produced by heating infusible precipitate with a dilute solution of ammonium chloride, nearly saturated with mercuric chloride, at 100° for one or two hours. The solution is filtered and allowed to cool, when the compound separates in the form of a fine, white powder.

Group III.

Brief reference may be made to some work on boron and some of its compounds.[19] The usual methods for the preparation of this element by the reduction of the oxide or chloride by metals are unsatisfactory, since the product invariably contains boride. The purest boron is obtained by the reduction of boron trichloride with hydrogen in the high tension electric arc. A new boron nitride, probably B_3N, has been prepared by heating boric acid with magnesium nitride. The ordinary nitride, BN, is conveniently obtained from boric acid and calcium cyanamide. When the vapour of boron trichloride is passed over red phosphorus in the presence of oxygen, a phosphate is formed having the formula $2B_2O,P_2O_5$, and other phosphates also appear to exist.

[19] W. Kroll, *Zeitsch. anorg. Chem.*, 1918, **102**, 1 ; *A.*, ii, 109.

Group IV.

Following on his work on the hydrides of boron, Stock, during the past three years, has undertaken the investigation of the hydrides of silicon. The following nomenclature of these compounds has been adopted.[20] The saturated compounds are termed silanes, the various members being differentiated thus: SiH_4 monosilane, Si_2H_6 disilane, Si_3H_8 trisilane, etc. The names of the other silicon compounds are derived from these in the usual rational manner of organic nomenclature. Thus Si_2H_4, Si_2H_2, would be termed disilene and disiline respectively. The oxygen derivatives are named siloxanes; thus SiH_2O protosiloxane (oxomonosilane) and $(SiH_3)_2O$ disiloxane.

The silanes have been obtained by the action of acid on magnesium silicide, the yield depending on the manner in which the substance has been prepared.[21,22] The best conditions are gained by using magnesium and silica in the proportions of 2:1, the latter substance being obtained by heating the hydrated compound. The hydrated silica should contain 0·3—0·5 per cent. of impurities, because this prevents the dehydrated substance from being too finely divided. About 100 grams of the mixture are used, and after the reaction has commenced the crucible is covered with a lid through which hydrogen is passed until the mass has cooled. The product is a blue, crystalline mass.

It is important that the silicide should be treated directly with acid, and not first to add water, since the silanes are extremely readily acted on by alkali. The gases evolved are washed with water, dried with calcium chloride and phosphoric oxide, and then condensed in a tube cooled by liquid air. By careful fractionation the first four silanes are obtained in a pure state, the sparingly volatile residue probably consisting of pentasilane, Si_5H_{12}, and hexasilane, Si_6H_{14}. About one-quarter of the silicon present as silicide is obtained in the form of hydrides, the remainder being converted into "silico-oxalic acid."

Monosilane, SiH_4, melts at $-185°$ and boils at $-112°/760$ mm. It is a colourless gas which is very stable at the ordinary temperature, and its spontaneous inflammation in the air is uncertain, small bubbles, as a rule, failing to catch fire. The

[20] A. Stock, *Ber.*, 1916, **49**, 108; *A.*, 1916, ii, 319.

[21] A. Stock and C. Somieski, *ibid.*, 111; *A.*, 1916, ii. 319; *ibid.*, 1917, **50**, 1739; *A.*, ii, 110; *ibid.*, 1918, **51**, 989; *A.*, ii, 361.

[22] A. Stock, C. Somieski, and R. Wintgen., *ibid.*, 1917, **50**, 1754, 1764; *A.*, ii, 110, 111.

presence of other hydrides of silicon causes it invariably to inflame. The vapour density at 19° is 16·02.

Disilane, Si_2H_6, melts at $-132\cdot5°$ to a liquid which boils at $-15°/760$ mm. It can be preserved unaltered at the ordinary temperature, but decomposes rapidly at 300°. The gas inflames in the air sometimes with violent explosion. It is very readily soluble in benzene or carbon disulphide, but the latter solution is spontaneously inflammable in air. With chloroform and carbon tetrachloride, vigorous reactions occur accompanied by flame. The vapour density of disilane at 21° is 31·7.

Trisilane, Si_3H_8, is a crystalline solid melting at $-117°$ to a colourless, mobile liquid, and boiling at $53°/760$ mm. It is much less stable than silane and disilane, decomposing at the ordinary temperature. The reaction with carbon tetrachloride is even more violent than in the case of disilane.

Tetrasilane, Si_4H_{10}, melts at $-93\cdot5°$ to a colourless liquid boiling at $80—90°/760$ mm., and having a vapour density of 61·0. The stability is less than that of trisilane, for tetrasilane decomposes fairly rapidly at the ordinary temperature.

The two first members of the series were analysed by the measurement of the hydrogen evolved by the action of concentrated sodium hydroxide solution, the chemical changes being expressed by $SiH_4 + 2NaOH + H_2O = Na_2SiO_3 + 4H_2$ and $Si_2H_6 + 4NaOH + 2H_2O = 2Na_2SiO_3 + 7H_2$. The composition of the other hydrides was proved by decomposition by slow passage through a quartz tube at 800—900°.

The reaction between silane and bromine is very violent, but if an excess of the gas is led into a vessel maintained at $-80°$ to $-70°$, on the walls of which solid bromine is deposited, the reaction can be controlled. In this way, the mono- and di-substituted derivatives have been obtained.

Bromomonosilane, SiH_3Br, melts at $-94°$ and boils at $1\cdot9°/760$ mm., forming a colourless gas. It may be preserved over mercury for some time, but it detonates on exposure to the air, giving silicic acid and brown silicon. With concentrated sodium hydroxide solution, it reacts according to the equation $SiH_3Br + 3NaOH = 3H_2 + NaBr + Na_2SiO_3$.

Dibromomonosilane, SiH_2Br_2, melts at $-70\cdot1°$ to a colourless, mobile liquid, and boils at $66°/760$ mm. It inflames in the air and is very sensitive to moisture, being decomposed into hydrogen bromide and a solid, $(SiH_2O)_x$. With alkali, it reacts as follows: $SiH_2Br_2 + 4NaOH = 2H_2 + 2NaBr + Na_2SiO_3 + H_2O$. When bromomonosilane is shaken with water, it gives disiloxane, $(SiH_3)_2O$. This is a colourless, odourless gas which does not inflame spontaneously,

but burns with a brilliant light, giving a white smoke and a deposit of brown silicon. It melts at $-144°$ and boils at $-15·2°/$ 760 mm., these constants being lower than those of the parent disilane. This is the reverse of that observed with dimethyl ether and ethane.

With water, disiloxane soon reacts to give hydrogen and insoluble compounds, like $(SiH_2O)_x$, etc. With sodium hydroxide solution, the decomposition is complete, according to the equation $(SiH_3)_2O + H_2O + 4NaOH = 2Na_2SiO_3 + 6H_2$. Disiloxane reacts very vigorously with chlorine at $-125°$ to give hexachlorodisiloxane, but most of this decomposes according to the equation $4(SiCl_3)_2O = 2SiO_2 + 6SiCl_4$. Tetrachloromonosilane, $SiCl_4$, melts at $-68·7°$ and boils at $137°/760$ mm., whilst hexachlorodisiloxane melts at $-33°$ and boils at $137°/760$ mm.

It would appear that protosiloxane, SiH_2O. can be obtained by the action of water on dibromomonosiloxane, but it is very difficult to separate the compound from the hydrogen bromide which is formed at the same time. Furthermore, the substance polymerises to a white, amorphous solid, $(SiH_2O)_r$. This polymeride is stable at $300°$ in a vacuum, but it inflames in air or chlorine and reacts with sodium hydroxide according to the equation $(SiH_2O)_x + 2NaOH \longrightarrow 2H_2 + Na_2SiO_3$.

Lastly, a very remarkable reaction of the silanes may be noted in that with hydrogen bromide in the presence of aluminium bromide they give bromine substitution products. Thus silane gives very readily monobromo- and dibromo-silane according to the equations $SiH_4 + HBr = SiH_3Br + H_2$ and $SiH_4 + 2HBr = SiH_2Br_2 + 2H_2$. This method for the preparation of the lower bromides is better than the direct bromination of silane.

Some further work on the zirconyl salts mentioned in last year's Report may be described.[23, 24, 25] It appears that the usually accepted normal zirconium nitrate, $Zr(NO_3)_4,5H_2O$, does not exist, for all attempts to prepare it by evaporation of solutions of zirconium hydroxide in nitric acid, even in an atmosphere saturated with nitric acid fumes, resulted in the formation of normal zirconyl nitrate, $ZrO(NO_3)_2$, with either $2H_2O$ or $3·5H_2O$. When this salt is heated at $120°$ in the presence of nitric acid vapour, it loses water and nitric acid, giving the basic nitrate.

$$3ZrO(NO_3)_2,ZrO_2,7H_2O.$$
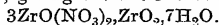
By heating the normal zirconyl nitrate in air, the following basic

[23] E. Chauvenet and Mlle. L. Nicolle, *Compt. rend.*, 1918, **166**, 781, 821 ; 4., ii, 234.

[24] E. Chauvenet and Mlle. H. Gueylard, *ibid.*, **167**, 24, 126 ; *A.*, ii, 269, 321.

[25] P. Bruère and E. Chauvenet, *ibid.*, 201 ; *A.*, ii, 321.

salts are formed: $2ZrO(NO_3)_2,ZrO_2,7H_2O$, $ZrO(NO_3)_2,2ZrO_2,4H_2O$, $ZrO(NO_3)_2,7ZrO_2,5H_2O$, and $ZrO(NO_3)_2,10ZrO_2,4H_2O$. An aqueous solution of the normal zirconyl nitrate slowly undergoes hydrolysis, giving a precipitate having the composition $ZrO(NO_3)_2,ZrO_2,nH_2O$.

Normal zirconyl sulphate forms compounds of the types $(ZrOSO_4)_3,X$ and $(ZrOSO_4)_3X_2$, where X is either ZrO_2, Na_2SO_4, K_2SO_4, or $(NH_4)_2SO_4$. The following have been isolated: $(ZrOSO_4)_3,K_2SO_4,8H_2O$, $(ZrOSO_4)_3,Na_2SO_4,7H_2O$, and
$$(ZrOSO_4)_3,2(NH_4)_2SO_4.7H_2O.$$

Evidence has also been found for the existence of the following double salts of acid zirconyl sulphate: $2(ZrOSO_4,SO_3),3Na_2SO_4$, $3(ZrOSO_4,SO_3),2Na_2SO_4$, $ZrOSO_4,SO_3(NH_4)_2SO_4$, and
$$ZrOSO_4,SO_3,2(NH_4)_2SO_4.$$
The first two salts have also been obtained with $8H_2O$ and $7H_2O$ respectively.

If the tetra-ammonia derivative of zirconium chloride, $ZrCl_4,4NH_3$, is heated at $350°$, it is converted into zirconium nitride, Zr_3N_4. The formulæ Zr_3N_x and Zr_2N_3 put forward by earlier workers are incorrect.

In last year's Report attention was directed to the remarkable analogy between the new oxychloride of zirconium therein described, $Zr_5O_8Cl_4,22H_2O$, and the basic chloride of tin, $Sn_5O_8Cl_4,7H_2O$. and at the same time stress was laid on the necessity for systematisation of metastannic acid and its derivatives. Some new work on metastannic acid has been published which bears on this question to a certain extent.[26] The present work deals with the action of nitric acid on tin, and the products now reported differ somewhat from those usually believed to occur. If the nitric acid is diluted with $1·25—2$ volumes of water, the only product is stannous nitrate, and with more concentrated, and even undiluted, acid at $0—15°$, the formation of stannous nitrate can still be observed, accompanied by normal or basic stannic nitrate.

Stannic nitrate even at the ordinary temperature slowly changes to the meta-salt. At $45°$, the change is so rapid that the solution suddenly gelatinises, and, after prolonged heating at $100°$, the change is complete. The powder obtained by the oxidation of tin with hot nitric acid, commonly called metastannic acid, is really a nitrate of metastannic acid, which on prolonged washing with water gives metastannic acid. The metastannic acid prepared in this way and dried in the air at the ordinary temperature has the composition $5H_2SnO_3,4H_2O$, the $4H_2O$ being lost on storage over

[26] A. Kleinschmidt, *Monatsh.*, 1918, **39**, 149 : *A.*, ii, 400.

sulphuric acid in a vacuum for several days. The statement is also made that parastannic acid. $H_2Sn_5O_{11},2H_2O$,[27] is only ordinary metastannic acid.

Metastannic acid reacts with hydrochloric acid and sulphuric acid to give easily hydrolysable compounds, and the resulting metastannyl chloride gives with sodium hydroxide the salt. $5SnO_2,Na_2O,4H_2O$. The nitrate of metastannic acid described above has the constitution $5SnO_2,2HNO_3,3H_2O$, whilst metastannyl chloride has the formula $5SnO_2,2HCl,3H_2O$.

It is preferable for the purpose of comparison to discuss the results given in this paper on the basis of Engler's formulæ. Thus the formula of sodium metastannate should be written
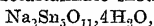
$$Na_2Sn_5O_{11},4H_2O,$$

and hence metastannic acid should be given the formula $H_2Sn_5O_{11},4H_2O$. The air-dried metastannic acid described in the above paper is therefore $H_2Sn_5O_{11},8H_2O$. which differs very little from that given by Engler. $H_2Sn_5O_{11},9H_2O$. Kleinschmidt entirely confirms Engler's results with sodium metastannate and with metastannyl chloride, $Sn_5O_9Cl_2,4H_2O$, but he has apparently isolated new salts in metastannyl nitrate, $Sn_5O_9(NO_3)_2,4H_2O$ and metastannyl sulphate, $Sn_5O_9SO_4,4H_2O$.

It must be confessed that, in view of the undoubtedly strong evidence brought forward by Engler in favour of the existence of parastannic acid and its derivatives, Kleinschmidt's statement that the para-acid is merely metastannic acid does not appear convincing. In the first place, Engler found air-dried metastannic acid to be $H_2Sn_5O_{11},9H_2O$, and air-dried parastannic acid to be

$$H_2Sn_5O_{11},7H_2O,$$
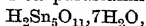
both losing $5H_2O$ on drying over sulphuric acid in a vacuum. Kleinschmidt finds air-dried metastannic acid to be $H_2Sn_5O_{11},8H_2O$, and possibly, therefore, he did not sufficiently differentiate between the two hydrates. In the second place, Engler obtained the chlorides and the sodium salts of the two acids and differentiated between them. In the third place, as pointed out by the writer in last year's Report, there seem to exist two series of basic zirconyl salts with the same relationship between them, as stated by Engler to exist between his metastannic and parastannic compounds.

It has been found possible to prepare the sub-chloride, sub-bromide, and sub-iodide of lead by the action of the corresponding methyl haloid on lead sub-oxide.[28] This oxide is obtained by heating lead oxalate in an exhausted tube at 270—370°, care

[27] R. C. Engler, *Compt. rend.*, 1897, **125**, 464 ; *A.*, 1897, ii, 29.

[28] H. G. Denham, *T.*, 1917, **111**, 29 ; 1918, **113**, 249.

being taken that the total pressure of the evolved gases does not exceed 5 mm. By the action of methyl iodide vapour at a maximum temperature of 262° on the sub-oxide. lead sub-iodide is obtained as a pure yellow powder. It has a solubility in water about one-ninth of that of the normal iodide, and the solution gives no precipitate with potassium chromate and only a slight darkening with hydrogen sulphide. On heating above 300°, the sub-iodide darkens in colour owing to decomposition to lead and lead iodide.

By analogous methods, the sub-chloride and sub-bromide of lead have been prepared as grey powders. Both are sparingly soluble in water, fairly stable in air, but easily oxidised by bromine water. Both salts are readily decomposed by acid into the normal salt and lead.

Group V.

A method has been described for the preparation of chemically pure antimony, the commercially pure metal not being satisfactory in this respect.[29] Antimony trichloride or pentachloride is purified by distillation and converted into chloroantimonic acid.[30] The chloride is dissolved in concentrated hydrochloric acid, and chlorine is passed in until the solution becomes greenish-yellow, and then hydrogen chloride is introduced. After purification by recrystallisation, the chloroantimonic acid is hydrolysed to antimonic acid, which is reduced to metal by fusion with potassium cyanide. The metal thus obtained is free from all impurities and melts at 630·3°.

Metallic antimony dissolves in a solution of sodium in liquid ammonia.[31] It would seem that there are at least two compounds formed, in one of which the atomic ratio Sb:Na is greater than 2:1, whilst in the other it is less than 2:1. Some electrolytic investigations show that the antimony is present in the solutions as anion, and that more than one atom of antimony is associated with each negative charge.

By the interaction of potassium aminosulphonate and hypochlorous acid in equivalent proportions in cold aqueous solution, potassium chloroaminosulphonate, $NHCl \cdot SO_3K$, is formed.[32] This salt may be isolated by evaporating the mixture to a small bulk, in a high vacuum, at as low a temperature as possible and precipitating with alcohol. It forms limpid, hygro-

[29] E. Groschuff, *Zeitsch. anorg. Chem.*, 1918, **103**, 164 ; *A.*, ii, 322.
[30] R. F. Weinland and H. Schmid, *ibid.*, 1905, **44**, 37 ; *A.*, 1905, ii, 326.
[31] E. B. Peck, *J. Amer. Chem. Soc.*, 1918, **40**, 335 ; *A.*, ii, 168.
[32] W. Traube and E. von Drathen, *Ber.*, 1918, **51**, 111 ; *A.*, ii, 108.

scopic crystals, and is comparatively stable. When warmed with mineral acids, the salt undergoes hydrolysis according to the equation· $NHCl·SO_3K + H_2O = NH_2Cl + KHSO_4$. The corresponding barium salt is not so stable, but potassium bromoaminosulphonate is very similar in its properties.

Group VI.

When diantipyryl selenoselenide, $R_2Se:Se$, was burnt in a bomb in oxygen under 25—30 atm. pressure, a white, amorphous deposit was formed adhering firmly to the walls of the crucible. This proved to be a new oxide of selenium approximating to the formula Se_8O_4.[33] The substance is almost insoluble in water, and is decomposed by boiling sodium-hydroxide, about one-third of the selenium being deposited in the elementary state, the remainder giving rise to sodium salts of selenium acids.

Ferrous selenate can readily be obtained by the action of a concentrated solution of selenic acid on ferrous sulphide.[34] A certain amount of the selenic acid is reduced by the hydrogen sulphide in accordance with the equation $3H_2S + H_2SeO_4 = Se + 3S + 4H_2O$, but this does not interfere with the application of the method. If the filtered solution is allowed to crystallise, monoclinic crystals of $FeSeO_4,7H_2O$, isomorphous with $FeSO_4,7H_2O$, are obtained. The double selenates of the type $M_2SeO_4,FeSeO_4,6H_2O$ are readily obtained in the case of ammonium, rubidium, and cæsium. The corresponding potassium salt crystallised at a temperature not much higher than $0°$, whilst at the ordinary temperature very small, monoclinic crystals of the dihydrated salt are formed.

Reference was made in last year's Report to the action of chromyl chloride on phosphorus trichloride or phosphorus tribromide in dry carbon tetrachloride solution, by which compounds of the type $CrOCl,POCl_3$ are formed. This work has now been extended to include a study of the action of chromyl chloride on phosphorus di-iodide, tri-iodide, pentachloride, and pentabromide.[35] In the case of the first three phosphorus haloids, simple additive compounds are precipitated containing one molecule of chromyl chloride and one molecule of the phosphorus haloid. No reaction similar to that occurring with phosphorus trichloride and phosphorus tribromide takes place. In the case of phosphorus penta-

[33] F. von Konek, *Ber.*, 1918, **51**, 872; *A.*, ii, 309.

[34] A. E. H. Tutton, *Proc. Roy. Soc.*, 1918, [A], **94**, 352; *A.*, ii, 193.

[35] H. S. Fry and J. L. Donnelly, *J. Amer. Chem. Soc.*, 1918, **40**, 418; *A.*, ii, 167.

bromide, no definite compound was formed, but a mixture, presumably of $CrO_2Cl_2.PBr_5$ and $CrOCl.POBr_3$, due, no doubt, to the partial dissociation of the phosphorus pentabromide in carbon tetrachloride solution.

The compound, $CrO_2Cl_2.PI_2$, is brown and very unstable in moist air. It is readily decomposed by water with liberation of iodine, and, after boiling, the solution contains phosphate, chromate, chloride, and iodide ions.

The compound, $CrO_2Cl_2.PI_3$, forms a purplish-red powder which reacts with water in accordance with the equation $2CrO_2Cl_2.PI_3 + 4H_2O = 4HCl + 4HI + 2CrPO_4 + I_2$, and the compound,

$$CrO_2Cl_2.PCl_5,$$
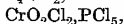
is a yellowish-red powder which readily decomposes in the air, evolving hydrogen chloride.

Considerable interest attaches to the preparation of a series of compounds of quinquevalent tungsten.[36] The starting point is the reduction of tungstic acid or a tungstate in oxalic acid solution with tin. The best results are obtained by reducing a solution of an alkali tungstate in a concentrated solution of oxalic acid containing slight excess of alkali oxalate. The course of the reduction can be followed by the colour change, through dark blue, green, and yellow to deep red. After removal of the tin and excess of oxalic acid, the complex oxalotungstite is precipitated by means of alcohol, and may be purified by dissolving in hot water and salting out, the sodium salt with sodium bromide and the potassium salt with potassium iodide. The salts must be dried in a current of carbon dioxide, but are fairly stable in air when dry. The sodium salt, $3Na_2O,2W_2O_5,4C_2O_3,12H_2O$, and the potassium salt, $3K_2O,2W_2O_5,4C_2O_3,9H_2O$, form red, crystalline powders which slowly oxidise in the air, and at $100°$ lose their water of crystallisation, but do not decompose. They are very readily soluble in water, but are insoluble in organic solvents.

The oxalotungstites dissolve in concentrated hydrochloric acid, forming a deep blue solution, which contains an oxychloride of quinquevalent tungsten, probably $WOCl_3$, because from this solution complex chlorides can be isolated containing $WOCl_3$ in combination with chlorides of the alkali metals or ammonium or hydrochlorides of organic bases. The ammonium and potassium salts are precipitated by saturating a hydrochloric acid solution of the corresponding oxalotungstite with hydrogen chloride. The rubidium, cæsium, aniline, tetraethyl- and tetrapropyl-ammonium compounds are precipitated when the corresponding chloride is added to a hydrochloric acid solution of an oxalotungstite. and the

[36] O. O. Collenburg, *Zeitsch. anorg. Chem.*, 1918, **102**, 247 ; *A.*, ii, 267.

pyridine and quinoline compounds are prepared by double decomposition of their hydrochlorides with ammonium chlorotungstite Four types of these complex chlorides have been observed. Type Ia has the composition M_2WOCl_5, in which M may be NH_4, Rb, Cs, or $C_6H_5NH_3$; type Ib, M_2WOCl_5,xH_2O, is represented by the potassium compound; type IIa, $MWOCl_4$, is represented by the pyridine and quinoline compounds; and type IIb, $MWOCl_4,H_2O$, by tetraethyl- and tetrapropyl-ammonium compounds. The compounds of type I form green crystals and correspond with the molybdenyl chlorides. The compounds of type II have no representative among molybdenum compounds; they form shining, brown crystals (IIa) or bright greenish-blue crystals (IIb).

The chlorotungstites are stable in dry air at the ordinary temperature, but decompose with oxidation to tungstates at 60—70°. They are immediately hydrolysed by water with formation of a brown hydroxide, which has not been analysed. They dissolve readily in absolute methyl or ethyl alcohol, with the exception of the rubidium and cæsium compounds, but not in other organic solvents. Concentrated hydrochloric acid and 35 per cent. sulphuric acid also dissolve them, but alkalis and ammonia decompose them.

The chlorotungstites react vigorously with a concentrated solution of potassium cyanide, with evolution of hydrogen cyanide. A reddish-yellow solution is formed containing cyanides of the type $M_4W(CN)_8$, from which a sparingly soluble cadmium compound, $Cd_2W(CN)_8,8H_2O$, has been isolated. A thiocyanic acid compound has also been isolated in the form of a pyridine salt having the composition $(PyH)_3WO(SCN)_5,xH_2O$.

Reference may be made to the important work on the nature and constitution of the heteropolytungstates and the heteropolymolybdates. The complexity of these compounds is at first sight somewhat confusing, but some fresh light has been thrown on them which has enabled them very definitely to be classified.[37] The nomenclature of these acids and their salts is based on the ratio between the numbers of the atoms of the non-metallic element and the metallic element (tungsten or molybdenum) in the complex anion. The fundamental type of the mononuclear acids is the 12-type with the general formula $H_{12-n}[R^n(M_2O_7)_6]$, where R is the non-metallic element of valency n and M is the metallic element. This type is the most stable of all these acids, and is formed in the presence of excess of the metallic acid. These acids form two series of hydrates, one of which crystallises in quadratic

[37] A. Rosenheim and J. Jänicke, Zeitsch. anorg. Chem., 1917, 101, 235 A., ii, 77.

octahedra with $28H_2O$, and the other in rhombohedra with $22H_2O$. The following have been prepared:

12-Borotungstic acid, $H_9[B(W_2O_7)_6],28H_2O$, forms two kinds of crystals, namely, large, transparent octahedra melting at 45—51°, and slender needles. A lower hydrate with $10H_2O$ was isolated. An iso-12-borotungstic acid, $H_9[B(W_2O_7)_6],22H_2O$, was obtained in the form of hexagonal, bipyramidal crystals.

12-Silicomolybdic acid, $H_8[Si(Mo_2O_7)_6],28H_2O$, forms transparent octahedra, which melt gradually at 47—55° to a uniform liquid. When crystallised from hot nitric acid, it forms a lower hydrate with $14H_2O$.

12-Silicotungstic acid crystallises with $28H_2O$ and with $22H_2O$, the transition point being at 28·5°.

12-Phosphomolybdic acid exists in yellow, octahedral crystals of the constitution $H_7[P(Mo_2O_7)_6],28H_2O$, and by crystallisation from hot nitric acid it is obtained in small, yellow, probably rhombohedral, tables with $22H_2O$.

12-Phosphotungstic acid forms crystals of the normal type with $28H_2O$ which, in the presence of traces of acid, break down into minute rhombohedra with $22H_2O$. The highest metallic salts which could be prepared of this acid were tribasic, for example, $Na_3H_4[P(W_2O_7)_6],13H_2O$, but in the guanidine salt,

$$(CN_3H_5)_7H_7[P(W_2O_7)_6]_2,12H_2O,$$
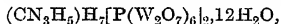
half the hydrogen is replaced.

12-Arsenotungstic acid could only be obtained in the form of its ammonium salt, $(NH_4)_5H_4[As(W_2O_7)_6],4H_2O$.

In addition to the above, unsaturated mononuclear acids have been prepared of the type $H_{12-n}[R^nO(M_2O_7)_5]$, their basicity being the same as that of the saturated acids.

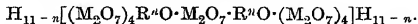10-Silicotungstic acid was obtained in the form of a potassium salt as cube-like crystals of the composition
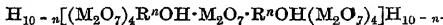
$$K_7H[SiO(W_2O_7)_5],11H_2O.$$
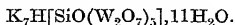
Turning to the binuclear acids, these form two groups, the 1:11 acids having an outer bridge,

$$H_7[R^n\cdot OH\cdot(M_2O_7)_5]\cdot M_2O_7\cdot[R^n\cdot OH\cdot(M_2O_7)_5]H_7,$$
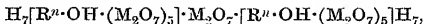
and the 1:9 (luteo-) acids an inner bridge,

$$H_{11-n}[(M_2O_7)_4R^nO\cdot M_2O_7\cdot R^nO(M_2O_7)_4]H_{11-n}.$$

The acids of the last type, it is suggested, are in tautomeric equilibrium with the form

$$H_{10-n}[(M_2O_7)_4R^nOH\cdot M_2O_7\cdot R^nOH(M_2O_7)_4]H_{10-n}.$$

11-Phosphotungstates are formed at an intermediate stage in the decomposition of 12-phosphotungstic acid by strong

They are stable salts which can be readily prepared from the barium salt, to which the constitution

$$Ba_7[P(OH)(W_2O_7)_5] \cdot W_2O_7 \cdot [(W_2O_7)_5(OH)P],53H_2O$$
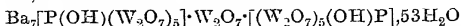
is given. The 11-arsenotungstates are completely analogous to the phosphotungstates.

9-Phosphotungstic acid, $P_2O_5,18WO_3,42H_2O$, forms thin, six-sided tables, which are very readily soluble and melt at 28°. Since all attempts to prepare salts of higher basicity than 5 failed, it was concluded that the constitution of this acid must be represented by the formula

$$H_5[P(OH)(W_2O_7)_4 \cdot W_2O_7 \cdot (W_2O_7)_4(OH)P]H_5.36H_2O.$$
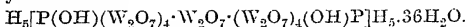
The silver salt, $5Ag_2O,P_2O_5,18WO_3,34H_2O$, is precipitated as yellow, amorphous flakes, which quickly crystallise.

9-Arsenotungstic acid corresponds exactly with the 9-phosphotungstic acid. Only the tribasic potassium and ammonium salts were prepared, these having similar properties to the tribasic salts of the phosphotungstic acids.

Still more complex heteropoly-acids have been studied which probably contain four nuclei, but no constitutional formulæ have as yet been suggested for them.

Group VIII.

Some years ago, an account was published of the preparation and properties of the nitrosopentamminecobalt salts.[38] Two series of salts were described, one being red and the other black. Both series were obtained by the action of nitric oxide on ammoniacal solutions of cobalt salts and have the same general formula, $NO \cdot Co(NH_3)_5 \cdot X_2$, the two series being considered to be valency isomerides. This work has been repeated, and it is now claimed that whilst the earlier statements with respect to the black series are correct, most of the statements with respect to the red series are incorrect.[39]

These salts present considerable interest from the point of view of valency and also from the point of view of their constitution. Whereas the black series has the simple constitution as stated above, the red series must be considered as having the general formula

$$(N_2O_2) \!<\! {Co(NH_3)_5X_3 \atop Co(NH_3)_5X_2},$$
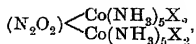
[38] J. Sand and O. Genssler, *Ber.*, 1903, **36**, 2083 ; *A.*, 1903, ii, 549 ; *Annalen*, 1903, **329**, 194 ; *A.*, 1904, ii, 39.

[39] A. Werner and P. Karrer, *Helv. Chim. Acta*, 1918, **1**, 54 ; *A.*, ii, 319.

and the question of the nature of the radicle, N_2O_2, is as yet un-decided. By the action of acids, the radicle is split off as hypo-nitrous acid, $H_2N_2O_2$, which, however, immediately decomposes, giving nitrous oxide. It was not found possible to isolate the hyponitrous acid or to detect it in solution. Attempts were made to prepare the red salts by the action of silver hyponitrite on chloropentamminecobalt salts, but they were unsuccessful, aquo-pentamminecobalt salts being obtained.

Some of the new salts now described may be noted.

Black nitrosopentamminecobalt iodate, $NO \cdot Co(NH_3)_5(IO_3)_2$, is precipitated as a blackish-brown, crystalline powder when nitric oxide is passed into a strongly ammoniacal solution of cobalt iodate.

Dinitrosodecamminedicobalt salts (red series), YX_4, where $Y = N_2O_2 \cdot Co_2(NH_3)_{10}$. The following members of this series may be mentioned: $YBr_4,3H_2O$, $YI_4,4H_2O$, $Y(SO_4)_2,2H_2O$, $Y(C_2O_4)_2,H_2O$, $Y(CrO_4)_2,4H_2O$; in addition to these, several acid salts have been obtained. Many of the red salts described by the earlier authors are now stated not to exist.

Definite compounds have been prepared of osmium tetroxide with the hydroxides of potassium, rubidium, and cæsium, and in this way the tetroxide is proved to possess an acid function.[40] The potassium compound, $OsO_4,2KOH$, the rubidium compound, $OsO_4,RbOH$, and the two cæsium compounds, $OsO_4,CsOH$ and $2OsO_4,CsOH$, all form orange or brown crystals, and are readily soluble in water, in which solution they are strongly hydrolysed.

Mention may also be made of the fact that osmium tetroxide is reduced by concentrated hydrochloric acid according to the equa-tion $2OsO_4 + 12HCl = 2OsO + 6Cl_2 + 6H_2O$.[41]

<div style="text-align: right">E. C. C. BALY.</div>

[40] L. A. Tschugaev, *Compt. rend.*, 1918, **167**, 162; *A.*, ii, 322.
[41] J. Milbauer, *J. pr. Chem.*, 1917, [ii], **96**, 187; *A.*, ii, 202.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

IT is not improbable that the Annual Reports are subjected to more criticism than the publications out of which they are constructed, but possibly on the present occasion sympathy will be accorded both to the reviewers and to those who, during an exceptional year, have striven to preserve theoretical and disinterested research. Due appreciation of research demands full recognition of the conditions, material and otherwise, under which the work is done, and consequently one ought not to labour the obvious and condemn the progress recently made in aliphatic chemistry as trivial. Much original ability has, of necessity, been directed into other channels, so that publications have been reduced both in number and quality, but there is no reason why this should be regarded as a symptom of intellectual famine. On the contrary, there are many signs, amongst which may be included the advent of new periodicals, that research work is entering on a wider and more active phase.

In compiling this section of the present Report, an attempt has been made to preserve the form adopted in recent years, and to make the narrative continuous. In some cases it has been difficult to resist the temptation of trying to make a modest ration go as far as possible so as to avoid the appearance of dealing preferentially with favourite topics, but although the different branches of the subject are treated in varying detail, the space allocated to each heading is roughly proportional to the amount and standard of the work to be discussed.
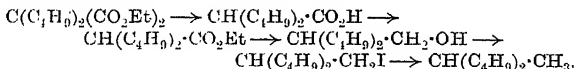
Throughout the year the writer has been encouraged in his task by the hope that the Report would be studied by those who were returning with fresh zeal to interrupted scientific work. If this hope is realised, such readers are unlikely to be critical, and the writer will be amply rewarded.

Hydrocarbons.

The most outstanding publications on aliphatic hydrocarbons which have appeared during the period embraced within the current

Report are concerned with the effects of temperature and pressure on the limits of inflammability of air–methane mixtures. The nature and treatment of this important topic place the work beyond the scope of the present section, but the latest contributions [1, 2, 3] to this systematic series of researches should not remain unnoticed. In recent years much of the synthetical and descriptive work on open-chain hydrocarbons has emanated from Russia, and in default of continued publications from this source, there is comparatively little to report under the above heading. It is, in fact, mainly with the idea of preserving the subdivision adopted in previous Reports that a separate section is now devoted to hydrocarbons.

Mention should be made of the synthesis of tertiary hydrocarbons,[4] which has been commenced by Levene as a preliminary to the study of the oxidation of these compounds. The methods employed are for the most part orthodox. Thus, in the particular synthesis which has been carried to a completion a start was made from ethyl dibutylmalonate, $C(C_4H_9)_2(CO_2Et)_2$, from which α-butyl-hexoic acid, $CH(C_4H_9)_2 \cdot CO_2H$, was obtained in the usual way. From this, the corresponding ethyl ester was prepared and reduced to give α-butylhexyl alcohol. Subsequent conversion into the corresponding iodide, followed by reduction with zinc and acetic acid, ultimately yielded β-butylhexane. The essential steps are outlined below:

$$C(C_4H_9)_2(CO_2Et)_2 \longrightarrow CH(C_4H_9)_2 \cdot CO_2H \longrightarrow$$
$$CH(C_4H_9)_2 \cdot CO_2Et \longrightarrow CH(C_4H_9)_2 \cdot CH_2 \cdot OH \longrightarrow$$
$$CH(C_4H_9)_2 \cdot CH_2I \longrightarrow CH(C_4H_9)_2 \cdot CH_3.$$

The most important experimental feature of the above synthetical scheme is the reduction of the ester to the corresponding alcohol, this process having been effected by means of sodium.

Although the ultimate objective in an important paper, to which attention is now directed, was the accumulation of evidence bearing on the technical refining of petroleum oils, a number of useful generalisations have been made on the action of sulphuric acid on olefines.[5] On the results of a large number of comparative tests, it is shown that the formation both of alcohols and of alkyl sulphates is profoundly affected by the electrochemical character of the substituting groups introduced into the parent ethylene molecule. Another generalisation which emerges is that polymerisation of

[1] W. Mason and R. V. Wheeler, *T.*, 1918, **113**, 45.

[2] W. Payman and R. V. Wheeler, *ibid.*, 656.

[3] R. V. Wheeler, *ibid.*, 840.

[4] P. A. Levene and L. H. Cretcher, jun., *J. Biol. Chem.*, 1918, **33**, 505 ; *A.*, i, 250.

[5] B. T. Brooks, and I. Humphrey, *J. Amer. Chem. Soc.*, 1918, **40**, 822 ; *A.*, i, 286.

ethylenic hydrocarbons by the agency of sulphuric acid becomes more pronounced as the molecular weight of the olefine increases. It is ·pointed out in view of this observation that the identification of polynaphthenes in hydrocarbons which have been purified by treatment with sulphuric acid is not conclusive evidence of the existence of these compounds in the original petroleums. The investigation now under review also includes an examination of the conditions under which alcohols are formed directly by the action of diluted sulphuric acid on ethylene, and the work is stamped as commendable in that a difficult technical problem has been attacked by systematic, if laborious, methods, giving results of very general interest.

A brief reference may be introduced here to a few new observations concerning compounds closely related to simple hydrocarbons. The fact that the reaction between carbon tetrabromide and silver fluoride takes place in definite stages to give the complete series of intermediate fluorobromo-derivatives is only noteworthy in view of the drastic conditions necessary to complete the fluorination.[6] This difficulty will not come as a surprise to those who have had frequent occasion to displace one halogen by another even in aliphatic compounds of the simplest type. Then again, as halogen compounds are frequently used as solvents in exact measurements, it may be noted that chloroform is comparatively unstable under the. influence of ultra-violet radiation,[7] and, further, that trichloroethylene is on occasions a somewhat fickle solvent, on account of its tendency to disengage hydrogen chloride.[8] It is well to recognise these properties before entrusting to the solvents valuable material which is easily hydrolysed by traces of acids.

Practical details have also been contributed [9] of a variation in the preparation of chloroform from alcohol, and these should find application in the teaching laboratory, and thus introduce economy into a preparation which, in the hands of elementary students, is notoriously wasteful.

Alcohols and their Derivatives.

Practically all the publications on aliphatic alcohols have been concerned with pyrogenic changes, or with the reactions which hydroxyl compounds undergo at moderate temperatures in the presence of catalysts. Taking the particular case of ethyl alcohol, it

[6] H. Rathsburg, *Ber.*, 1918, **51**, 669 ; *A.*, i, 333.

[7] A. Kailan, *Monatsh.*, 1917, **38**, 537 ; *A.*, i, 209.

[8] W. Elsner, *Chem. Zeit.*, 1917, **41**, 901 ; *A.*, i, 210.

[9] K. Ukita, *J. Chem. Ind., Tokyo*, 1918, **21**, 219 ; *A.*, i, 333.

is, of course, well known that the decomposition promoted by the agency of metals or of metallic oxides may follow two alternative routes, leading respectively to (a) ethylene and water, or (b) acetaldehyde and hydrogen. Determination of the ratio $C_2H_4 : H_2$ in the evolved gases thus gives an index of the partition between these two rival reactions.

In a study [10] of the relative effects of various catalysts on alcohols it is shown that, as was to be expected, the presence of water vapour is favourable to the formation of acetaldehyde, and, conversely, that the addition of hydrogen to the gaseous alcohol increases the proportion of ethylene. That the effect of water vapour is a serious factor in these reactions is also indicated by the results obtained in a daring attempt to examine the products formed when glycerol is subjected to various types of catalytic decomposition.[11] Considering the possibilities which are open, however, the products actually isolated are surprisingly simple. Thus the effect of passing glycerol vapour over heated alumina is to produce acraldehyde, whilst, in the presence of finely divided copper, ethyl and allyl alcohols are formed. With uranous oxide, on the other hand, both the above alcohols are produced, together with some acraldehyde, and the combined results furnish a good example of the application of catalytic processes to compounds of great reactivity without encountering the complete· molecular breakdown which might reasonably have been predicted.

Although it is well known that the action of phosphorus haloids on polyhydroxy-compounds is extremely complex, the fact that simple monohydric alcohols frequently react abnormally is not so generally recognised. In the course, however, of examining the formation and reactions of alkyl phosphites, new facts have come to light which serve to clear up a number of difficulties. When phosphorous chloride acts on an alcohol, the reactions which ensue involve the successive formation and decomposition of the complete series of alkyl phosphites.[12] The three consecutive reactions are thus $PCl_3 + 3R·OH = P(OR)_3 + 3HCl \longrightarrow OH·P(OR)_2 + RCl \longrightarrow OR·P(OH)_2 + RCl \longrightarrow P(OH)_3 + RCl$, and, according to the experimental conditions, the reaction may be approximately arrested at any desired stage. In an extension [13] of the work a detailed account is given of the stability of dialkyl phosphites. These compounds, as was to be expected, are found to be neutral towards indicators and

[10] C. J. Engelder, *J. Physical Chem.*, 1917, **21**, 676 ; *A.*, ii, 13.

[11] P. Sabatier and G. Gaudion, *Compt. rend.*, 1918, **166**, 1033 ; *A.*, i, 334.

[12] T. Milobendzki and A. Sachnowski, *Chemik Polski*, 1917, **15**, 34 ; *A.*, i, 477.

[13] *Ibid.*, 48 ; *A.*, i, 478.

are poor conductors, but nevertheless are capable of forming metallic salts by somewhat indirect methods.[14]

Aldehydes and Ketones.

Although good working methods are available for preparing the lower aliphatic aldehydes, practical difficulties quickly intervene which place limitations on processes depending on the catalytic dehydrogenation of alcohols, and the synthetic organic chemist will welcome a new method[15] in which aldehydes can be conveniently prepared from the corresponding acyl chlorides. The reduction is carried out catalytically, a stream of hydrogen being passed through a boiling solution of the chloride in an indifferent solvent, such as xylene. These energetic conditions do not seem to affect the catalyst, which may be either barium sulphate coated with palladium or the particular form of nickel recommended by Kelber. Experimental details are quoted which lead to the opinion that the process possesses a high degree of efficiency. The fact that butaldehyde has in this way been obtained in 50 per cent. yield from butyryl chloride is perhaps not in itself a specially striking example of its merits, but the method can evidently be applied successfully to the preparation of aromatic hydroxy-aldehydes,[16] and there seems no reason why it should not be equally applicable to the production of substituted aldehydes of the aliphatic series.

For a considerable time the hope has been entertained that acetaldehyde may prove to be a starting point in the preparation of many compounds of varied type, and, naturally enough, attention is still being directed to improving the methods of obtaining the compound from acetylene.[17] Some indication of the potential value of acetaldehyde is given in a paper[18] which describes its catalytic conversion into crotonaldehyde by the action of uranium oxide at 360°. The product can thereafter be easily reduced by means of nickel to give n-butyl alcohol, and the further fact emerges that, during the crotonisation of acetaldehyde, a certain amount of higher homologues is formed. This observation at once opens out wide possibilities.

With regard to ketones, few points of general interest have been noted, but reference should be made to two papers dealing with the

[14] T. Milobendzki and M. Szwejkowska, *Chemik Polski*, 1917, **15**, 56; *A.*, i, 479.
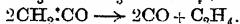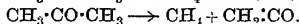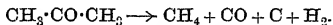
[15] K. W. Rosenmund, *Ber.*, 1918, **51**, 585; *A.*, i, 300.

[16] K. W. Rosenmund and F. Zetzsche, *ibid.*, 594; *A.*, i, 300.

[17] H. Dreyfus, *Brit. Pat.*, 105064; *A.*, i, 251.

[18] P. Sabatier and G. Gaudion, *Compt. rend.*, 1918, **166**, 632; *A.*, i, 251.

chemistry of acetone, which, in view of existing conditions, ought not to remain unmentioned. Although the production of acetone by the dry distillation of calcium acetate is now a process which has been brought to a remarkable state of efficiency, the reactions involved are complex and the by-products are numerous. In particular, the formation of gases represents a serious loss of acetone, and information indicating the conditions under which these by-products are produced is somewhat scanty. It has been shown, however,[19] that when acetone is heated with lime at temperatures ranging up to 630°, a species of "cracking" occurs, which results in the formation of methane, ethylene, hydrogen, carbon monoxide, and carbon dioxide. As the temperature is raised to the upper limit mentioned, the amount of methane increases rapidly, whilst that of hydrogen is diminished. The explanation put forward is that acetone undergoes (a) a high temperature dissociation, and (b) conversion into keten, which thereafter decomposes:

$$CH_3 \cdot CO \cdot CH_2 \longrightarrow CH_4 + CO + C + H_2.$$
$$CH_3 \cdot CO \cdot CH_3 \longrightarrow CH_4 + CH_2 \text{:} CO.$$
$$2CH_2 \text{:} CO \longrightarrow 2CO + C_2H_4.$$

This scheme can be expanded to account fairly well for the known products which accompany acetone during manufacture by the dry distillation method, particularly when the influence of metals in promoting further catalytic changes is taken into account. The experimental conditions adopted in the research now under discussion are, moreover, those which are liable to be reproduced in large-scale working. It is obviously a difficult problem to minimise the production of gas in the manufacture of acetone, but evidently the exclusion of air and the limitation of the temperature to the lowest working minimum during dry distillation are essential factors.

As the standard tests for the purity of acetone depend on the use of alkaline potassium permanganate, interest is attached to a paper which deals with the mechanism of the reactions involved.[20] It has long been known that, in the absence of alkali, pure acetone is not appreciably attacked by permanganate, and it now appears that the oxidation of the ketone in an alkaline system follows a different route according to the amount of alkali added. In order to account for the fact that the essential oxidation products are acetic and oxalic acids together with carbon dioxide, it is suggested that

[19] M. E. Freudenheim, *J. Physical Chem.*, 1918, **22**, 184 ; *A.*, i, 252.
[20] E. J. Witzemann, *J. Amer. Chem. Soc.*, 1917, **39**, 2657 ; *A.*, i, 58.

the oxidation process involves preliminary enolisation of the acetone, followed by the formation of pyruvic acid :

$$COMe_2 \qquad CH_2{:}CMe{\cdot}OH \qquad HO{\cdot}CH_2{\cdot}CMe(OH)_2$$
$$CHO{\cdot}CMe(OH)_2 \longrightarrow CO_2H{\cdot}CMe(OH)_2 -$$
$$\longrightarrow CH_3{\cdot}CO_2H + CO_2$$

$$CH_3{\cdot}CO{\cdot}CO_2H$$

$$CH_2{:}C(OH){\cdot}CO_2H \qquad C_2O_4H_2 + CO_2.$$
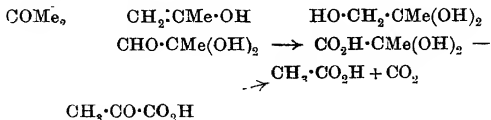
The above scheme is in agreement with the general observation that the ketones which are attacked most readily by permanganate are those which are most liable to assume the enolic condition and to give dibasic acids on oxidation. The paper is one which will be read with interest by all who are concerned with the examination and testing of acetone.

Results which may ultimately prove of considerable value in synthesis have been obtained in a study of the reaction between mesityl oxide and hypochlorous acid.[21] On general grounds it might have been expected that phorone derivatives would be formed, but the simple ketochlorohydrin, $OH{\cdot}CMe_2{\cdot}CHCl{\cdot}COMe$, proved to be the essential product. Under the influence of dehydrating agents this passes into the unsaturated chloro-ketone, which in turn can be transformed into the corresponding substituted ethylene oxide :

$$CMe_2{:}CCl{\cdot}COMe \qquad O{<}^{CMe_2}_{CH{\cdot}COMe}.$$
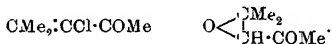
A number of synthetic possibilities are thus opened out, but it will be well to delay speculation regarding the future of this reaction until evidence is available confirming the above formulæ.

Acids and their Derivatives.

Current researches on acids show a tendency to focus on problems of constitution, and it is well that this should be the case, considering the suspicion with which the standard representation of the carboxyl group is now regarded. Before referring to a fresh discussion on this subject contributed by Hantzsch, it may be advisable to mention briefly an introductory paper[22] which deals with some general principles.

A review of past work on the optical absorption method of determining keto-enol equilibria shows that the results are but little

[21] K. Slawiński, *Chemik Polski*, 1917, **15**, 106 ; *A.*, i, 481.
[22] A. Hantzsch, *Ber.*, 1917, **50**, 1413 ; *A.*, ii, 2.

affected by the formation of additive compounds between the solvent and the solute, provided such addition does not occasion profound structural changes. Several examples are quoted in support of this view, for which an approximate parallel can frequently be found in the analogous phenomenon of optical activity. With regard to the special case of acids, it is pointed out that the ethereal salts of a fatty acid show identical optical absorption, and the same holds true for the alkali and alkaline earth-salts. In the particular example of trichloroacetic acid,[23] it is interesting to note that when dissolved in such diverse solvents as water and light petroleum, the optical properties of the compound remain constant and are identical with those of the alkali salts in aqueous solution. On the other hand, different absorption curves are given by alcoholic solutions of the acid, but here again these results are duplicated by solutions of the esters in indifferent solvents. A common expression must thus be found for the salts and for the free acid, and this, according to Hantzsch, is given by the following structures in which the ionisable fractions are represented as attached to two oxygen atoms:

$$\text{Acid.} \qquad\qquad \text{Salt.}$$

$$R\cdot C\!\!<^O_O \Big\} H \qquad\qquad R\cdot C\!\!<^O_O \Big| M$$

Accepting the above view, the conventional expressions $R\cdot CO\cdot OH$ and $R\cdot CO\cdot OM$ are reserved for "pseudo-acids" and "pseudo-salts" respectively. It would be inadvisable at this stage to express an opinion on the above suggestions or to subject them to detailed criticism. Some difficulty has evidently been experienced in extending the principles to examples other than that of trichloroacetic acid, and the experimental results do not agree uniformly with the theory which, it may be remarked, is at variance with the results of other and no less comprehensive work on the structure of aliphatic esters and acids.

Considerable interest is attached to the systematic efforts now being made by Böeseken and his pupils to extend the conductivity method of ascertaining the constitution and configuration of hydroxy-compounds to the special case of substituted acids. The principle involved is that the addition of boric acid results in pronounced exaltation of the conductivity only when hydroxyl groups are attached to adjacent carbon atoms and lie on the same side of the plane of the carbon chain. Results are now described [24, 25] which
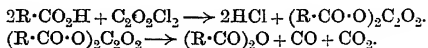
[23] A. Hantzsch, *Ber.*, 1917, **50**, 1422; *A.*, ii, 4.

[24] J. Böeseken and H. Kalshoven, *Rec. trav. chim.*, 1918, **37**, 130; *A.*, ii, 146.

[25] J. Böeseken and pupils, *ibid.*, 165; *A.*, ii, 146.

show that the method, which was first developed in the sugar group, is well adapted to the determination of the structure of aliphatic hydroxy-acids, although, naturally enough, it does not serve to discriminate between a simple racemic acid and its active components.[26]

The extended use to which oxalyl chloride has recently been put has resulted in the development of yet another method for preparing anhydrides.[27] So far, the process has been applied only to aromatic examples, but there seems no reason why it should not be equally applicable to aliphatic compounds. Apparently the reaction, which is conducted on the free acid, proceeds in the two stages shown below :

$$2R\cdot CO_2H + C_2O_2Cl_2 \longrightarrow 2HCl + (R\cdot CO\cdot O)_2C_2O_2.$$
$$(R\cdot CO\cdot O)_2C_2O_2 \longrightarrow (R\cdot CO)_2O + CO + CO_2.$$

The procedure is simple and the yields obtained are good. In special cases the intermediate mixed anhydride figured above can be isolated as an individual compound, and the reaction thus closely resembles the thionyl chloride method of preparing anhydrides, and may on occasions prove a convenient alternative.

Esters.

A large proportion of recent papers dealing with aliphatic esters is concerned with comparatively unimportant variations in working processes. In a few cases, however, publications which display no essential novelty are worthy of mention in view of the utility of the results described. All workers who have had occasion to prepare esters in a specially pure condition must have been struck with the variable "constants" quoted in the literature, and have been faced with the difficulty of recognising when any particular preparation conformed to the maximum standard of purity. Value is thus attached to a renewed effort [28] to determine the exact physical constants of a series of simple aliphatic esters. The data now quoted will be found useful for reference purposes, and it is to be hoped that the examination will be extended to a larger selection of cases.

Although methyl sulphate has been in use as an alkylating reagent for a considerable time, the exact mechanism of its

[26] J. Böeseken and L. A. van der Ent., *Rec. trav. chim.*, 1918, **37**, 179 ; *A.*, ii, 147.

[27] R. Adams, W. V. Wirth, and H. E. French, *J. Amer. Chem. Soc.*, 1918, **40**, 424 ; *A.*, i, 165.

[28] J. H. Mathews and K. E. Faville, *J. Physical Chem.*, 1918, **22**, 1 ; *A.*, 153.

behaviour has been studied only within the past year or two, and even now is imperfectly understood. As a result it is occasionally somewhat difficult to predict exactly the best conditions under which the reagent should be used. Some light is thrown on this question by the results of an interesting research,[29] in which it has been shown that, in the methylation of phenolic hydroxyl groups, the use of potassium hydroxide is inferior to that of sodium hydroxide, whereas, in ester formation, the best yields are obtained when potassium salts are used. The discrepancy is apparently due to the more pronounced hydrolytic effect of potassium hydroxide on dissolved methyl sulphate, and this reaction appears to be catalysed positively by potassium salts and negatively by sodium salts. This view has been indirectly supported by the results of an independent investigation,[30] in which the hydrolysis of methyl and ethyl sulphates in water and in dilute alkali is compared. In aqueous solution methyl sulphate is hydrolysed much more rapidly than the ethyl compound, and the difference in stability becomes greatly magnified in the presence of dilute potassium hydroxide. The possibility that this result is attributable to the unequal solubility of the two sulphates is excluded, and the conclusion is drawn that it is to be ascribed to the different mechanism of the reactions involved. In the paper referred to, it is noted as abnormal that whereas sodium methoxide reacts with methyl sulphate more readily than with ethyl sulphate, a methyl-alcoholic solution of sodium methoxide is less reactive towards methyl sulphate than an ethyl-alcoholic solution of sodium ethoxide. This observation does not stand alone, but it may be remarked that reactions involving metallic alkyloxides, alcohols, and esters are always complicated by an interchange of groups between the dissolved ester and the solvent, and the comparison instituted above has thus little significance.

Turning to problems connected with structure, it is evident that discussion of the keto-enol or aldehydo-enol isomerism of esters is by no means closed. In the case of the ethyl formylphenylacetates, some progress has been made in characterising the solid form (m. p. 110°) as the pure enolic variety. On the other hand, it is shown by means of titration by Meyer's method that the liquid isomeride contains after distillation about 9 per cent. of the aldehydic tautomeride.[31] Considering the fact that traces of alkali depress the melting points of the formylphenylacetates to a remarkable extent, it is difficult to attach much importance to the claim that the liquid and solid modifications of the enolic form are distinct chemical

[29] A. Klemenc [with E. Edhofer], *Monatsh.*, 1918, **38**, 553; *A.*, i, 220.
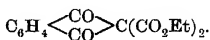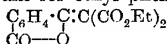[30] J. Pollak and A. Baar, *ibid.*, 501; *A.*, ii, 161.
[31] W. Dieckmann, *Ber.*, 1917, **50**, 1375; *A.*, i, 15.

individuals. Incidentally, it may be mentioned that the mixture of isomeric ethyl formylphenylacetates has been utilised in a synthesis of tropic acid,[32] the reduction being effected in neutral solution by the action of aluminium amalgam.

It would appear that a systematic effort[33] is now being made to revive the study of tautomeric change in esters by means of optical methods, special attention being paid to the variations in specific refraction and dispersion which accompany keto-enol transformation. These factors are selected in preference to molecular refractions, and the results confirm the idea that not only can the simple structures $\cdot CO \cdot CHR \cdot$ and $\cdot C(OH) \colon CR \cdot$ be definitely identified, but their relative proportions in mixtures may be estimated. In certain cases, however, the results are not so easily interpreted, as, for example, when a β-diketone undergoes tautomeric rearrangement. The two forms thus produced contain, respectively, the groupings $\cdot CO \cdot CHR \cdot COR'$ and $OH \cdot C \colon CR \cdot CR' \colon O$. and the presence of conjugation in the di-enol results in pronounced exaltation both in refraction and dispersion. This necessitates the standardisation of optical values in compounds containing typical conjugated systems, and the experimental determination of these reference factors is already well advanced. This revival and extension of Brühl's original proposals seems necessary in view of the steady accumulation of conflicting and contradictory results in the examination of desmotropic changes One useful application can already be recorded.[34] In last year's Report, an account was given of new views regarding the structure of the compound hitherto known as "ethyl diacetylmalonate," which has been shown to be, in reality, the normal acetate of enolic ethyl monoacetylmalonate. This raises the question if any authentic diacylmalonic esters exist, and in the particular case of the "dioxalomalonates," the compounds have been subjected to the optical test. The abnormally high values of the refraction and dispersion are found to be in better agreement with the view that in these examples, also, the compounds are enolic and not true diacyl derivatives.

Somewhat novel views regarding the structure of the succinylmalonic esters are expressed in a paper[35] which deals primarily with the corresponding phthalyl compounds. The alternative formulæ for ethyl phthalylmalonate.

$$\begin{array}{l} C_6H_4 \cdot C \colon C(CO_2Et)_2 \\ \quad\ \ | \quad\ \ | \\ \quad\ CO\text{---}O \end{array} \qquad\qquad C_6H_4 \!\!\begin{array}{l}<\!\!CO\\<\!\!CO\end{array}\!\!>\!C(CO_2Et)_2.$$

[32] E. Müller, *Ber.*, 1918, **41**, 252 ; *A.*, i, 223.

[33] K. von Auwers, *Annalen*, 1918, **415**, 169 ; *A.*, ii, 381.

[34] K. von Auwers and E. Auffenberg, *Ber.*, 1918, **51**, 1087 ; *A.*, i, 479.

[35] *Ibid.*, 1106 ; *A.*, i, 436.

are again considered, and, on the basis of physical measurements, preference is given to the older unsymmetrical constitution. By similar methods, the structure of ethyl succinylmalonate is likewise claimed to be unsymmetrical, and as this view has to be reconciled with the current opinion that succinyl chloride is symmetrical, an ingenious structural scheme, which overcomes this difficulty, is submitted in the original paper.

Much patient work has been devoted to studying the condensation reactions promoted between ethyl oxalate and substituted ethyl crotonates by potassium ethoxide, but the subject does not lend itself readily to synopsis. In the case of the reaction between the oxalic ester and ethyl β-aminocrotonate, the change is simple, and consists of the elimination of alcohol followed by enolisation of the product.[36] When, however, the aminocrotonate is replaced by the corresponding ethoxy-ester, a complex reaction ensues and three molecules of alcohol are removed:

$$CO_2Et \cdot CH{:}C(CH_3) \cdot OEt \\ + CO_2Et \cdot CO_2Et + EtOK \qquad CO_2Et \cdot C{<}^{C(OEt) \cdot CH}_{CO \quad C \cdot OK} + 3EtOH.$$
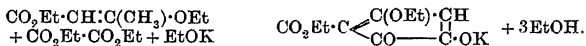
The potassium derivative thus produced undergoes a further interesting change when acidified, as the ethoxy-group is then eliminated, with the formation of the triketone.

$$CO_2Et \cdot CH{<}^{CO \cdot CH_2}_{CO \cdot CO}.$$
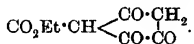
A compound of this nature offers considerable scope for possible enolisation, and a lengthy paper is devoted to a description of its somewhat complicated reactions.[37]

Optical Activity.

It is perhaps necessary to point out that, although the subject of optical activity has recently been dealt with at some length in this section of the Annual Reports, the treatment has not been comprehensive in that the policy has been followed of restricting discussion to new results furnished exclusively by aliphatic compounds. The writer is of the opinion that this policy, which was originally adopted to avoid the possibility of optical activity being relegated to "No Man's Land," should not in the future be rigidly adhered to, and that the scope should be sufficiently elastic to include observations on all types of optically active substances. On the present occasion, some overlapping with other sections of

[36] W. Wislicenus and K. Schöllkopf, *J. pr. Chem.*, 1917, [ii], **96**, 174 ; *A.*, i, 157.   [37] *Ibid.*, **95**, 269 ; *A.*, 1917, i, 700.

the Report is inevitable so as to include reference to a striking research which adorns the opening pages of the latest addition to periodical chemical literature.

The work of Werner and his school on the activity of cobalt-ammines has recently been expanded by the study of a series of compounds containing both cobalt and carbon asymmetric systems.[38] In directing attention to this development, it is felt that any attempt to discuss the results in an abbreviated form is liable to do injustice to an important piece of work, and the reader is referred to the original paper or the published abstract. The essential principle involved in the research is that the *cis*-type of the general compound $(XCo\ en_2)X$ can exist in two structural forms when one of the ethylenediamino-residues is replaced by an unsymmetrical diamino-group. This idea has been verified by the isolation of two series of *flavo*-salts (termed α and β) corresponding with the two structural varieties of the parent ammine, and also by the number of isomerides obtainable when the unsymmetrical diamino-component is likewise optically active. Taking the general case, where the asymmetric carbon and cobalt systems are represented, respectively, by A and B, the total number of optically active *flavo*-salts theoretically possible should be eight, as shown below:

$$\left.\begin{array}{l} d^lA\ .\ d\ B \\ d^lA\ .\ l\ B \\ l^lA\ .\ d\ B \\ l\ A\ .\ l\ B \end{array}\right\} \alpha \quad \text{and} \quad \beta.$$

These should exist in two groups of four, one series conforming to the α- and the other to the β-type. The experimental results obtained by Werner conform accurately to the prediction, and also include the isolation of the following partly racemic compounds:

1. Racemic with respect to A:

$$\left.\begin{array}{l} d+l\ A\ .\ d\ B \\ d+l\ A\ .\ l\ B \end{array}\right\} \alpha \quad \text{and} \quad \beta.$$

2. Racemic with respect to B:

$$\left.\begin{array}{l} d\ A\ .\ d+l\ B \\ l\ A\ .\ d+l\ B \end{array}\right\} \alpha \quad \text{and} \quad \beta.$$

The fact that, in addition, the two completely racemic compounds to which the above lead have likewise been obtained does not exhaust the results of a highly interesting research, the successful prosecution of which must have made exceptionally heavy demands on the experimenters concerned.

The painstaking and laborious work devoted during the past

[38] A. Werner, *Helv. Chim. Acta*, 1918, **1**, 5; *A.*, i, 375.

twenty-five years to the quantitative study of optical activity in carbon compounds has revealed many and unexpected complications, but, despite the fact that the ultimate goal is yet remote, investigators in this field do not allow their enthusiasm to flag. New results and fresh difficulties follow one another in quick succession, and it is highly desirable that, from time to time, the situation should be broadly reviewed. Bold speculation is needed if our ideas are to be saved from becoming stereotyped, and in recent years the pages of the Journal bear ample testimony to the fact that, in this respect, the subject is well served. There can be few more important issues in optical activity than the causes and mechanism of the Walden inversion, but work on this subject is restricted by the absence of any rigid tests whereby a change in configuration, as distinguished from a change in sign, can be detected with certainty. In this connexion, considerable importance must be attached to a recent paper in which an earlier series of researches on optically active α-hydroxy-acids has been extended to include α-amino-acids.[39] An attempt is made to lay down principles which would lead to the recognition of the configuration of similarly constituted compounds, and the literature of the subject has been thoroughly explored, so that the discussion is based on comprehensive evidence. It is with considerable reluctance that the writer of this section of the Report refrains from any attempt to give a condensed account of the work, but it is felt that any interference with the consecutive and closely reasoned argument would only lead to confusion.

Research on the effect of solvents in influencing optical inversions has now been applied to the important case in which bromine is displaced by the amino-group. It is found that in the particular case of *l*-phenylbromoacetic acid,[40] the amino-acid produced is opposite in sign when the displacement is carried out in aqueous or alcoholic solution. The results furnished by the lower alcohols are, however, in some measure irregular, in that considerable racemisation takes place in these solvents, and, in addition, it will be remembered that they do not occasion a change of sign when used as the media in which phenylchloroacetic acid is converted into phenylaminoacetic acid. The results contributed in this and the succeeding paper,[41] together with the discussion on the probable mechanism of the decomposition of halogen compounds, are of obvious importance in the synthesis of optically active amino-acids.

[39] G. W. Clough, *T.*, 1918, **113**, 526.
[40] G. Senter and S. H. Tucker, *ibid.*, 140.
[41] G. Senter, H. D. K. Drew, and G. H. Martin, *ibid.*, 151.

Turning to the related problems presented by racemisation phenomena, interest will be taken in new results which have been obtained in the phenylsuccinic acid series. In the particular case of compounds conforming to the tartaric acid type, change in configuration may give rise to either *meso*- or $d+l$-forms, the result in either case being regarded as racemisation. It has now[42] been established that the methyl and ethyl esters of r-diphenylsuccinic acid can, like the parent acid, be converted into the corresponding *meso*-varieties, and, further, that the active esters behave in a similar fashion. These changes are encountered during the process of partial hydrolysis, and the most striking feature of the results is the observation that the non-hydrolysed ester is largely racemised through conversion into the *meso*-form.[43] In fact, it appears that this is to be regarded as the principal source of the racemisation rather than the optical rearrangement of the liberated acids. As these results are not confined to any one type of compound, it can no longer be assumed that change in configuration involves of necessity the permanent removal of a group from an asymmetric system. This is already recognised, as a number of well-authenticated cases of auto-racemisation are now known, and the example presented by optically active benzoin may be cited as a case in point, but it is somewhat disconcerting to find another species of auto-racemisation extending to the case of esters.

It is a curious fact that some of the most striking results correlating the magnitude of specific or molecular rotation with constitution have been obtained with compounds of complex configuration. An additional example of this is furnished in a review of the optical activities displayed by polyhydroxy-acid amides, a number of new examples of this type of compound having been rendered available as a result of Weerman's work on the degradation of sugars. Comparison of their optical activities shows that the sign of the rotation of the amides is determined chiefly by the position of the hydroxyl group attached to the α-carbon atom, and is largely independent of the optical effect of the remaining asymmetric systems. When the formulæ are written as below, the product is dextrorotatory if the hydroxyl group is situated below the chain of carbon atoms, and is lævorotatory with the reverse configuration.

$$\overset{\text{H}}{\underset{\overset{|}{\text{OH}}}{\text{OH·CH}_2\text{·[CH·OH]}_n\text{·}\overset{|}{\underset{|}{\text{C}}}\text{·CO·NH}_2}} \qquad \overset{\text{OH}}{\underset{\overset{|}{\text{H}}}{\text{OH·CH}_2\text{·[CH·OH]}_n\text{·}\overset{|}{\underset{|}{\text{C}}}\text{·CO·NH}_2}}$$

Dextro.   Lævo.
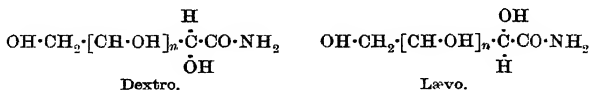
[42] H. Wren and C. J. Still, *T.*, 1917, **111**, 1019.

[43] H. Wren, *ibid.*, 1918, **113**, 210.

Accepting this view, which applies to cases other than those quoted by Hudson,[44] it is possible to ascribe a definite configuration to active hydroxy-acids where the α-carbon atom is asymmetric, and the evidence thus obtained supports Fischer's formula for d-tartaric acid, l-malic acid, and d-glyceric acid. Incidentally, the conclusions arrived at are in agreement with the configurations assigned by Freudenberg to malic and glyceric acids on the basis of the production of d-glyceric acid from l-isoserine.

This generalisation demands that one asymmetric system exerts a preponderating influence on the activity of a molecule which may contain asymmetric atoms, and that this is frequently the case is now recognised. Additional evidence pointing to the directing influence on rotation of one particular position in a molecule is also furnished by a recent paper [45] which deals exclusively with the special case presented by substitution in the benzene nucleus. Here, again, the generalisation emerges that the greatest optical effect is exerted when substituting groups are introduced in spatial proximity to the asymmetric carbon atom.

Carbohydrates.

During the past year, as has recently been the case, a considerable amount of work has been done on the preparation of various acetylated sugars.[46, 47] The methods employed show little or no departure from standard processes, but the work has been directed mainly to the isolation of pure stereochemical forms and to a study of the conditions under which these may be interconverted. In view of the discovery, to which reference was made in a previous Report,[48] that at least four definite galactose penta-acetates exist, research of this description acquires a new importance, and, in addition, the optical rotations of substituted sugars which are thus rendered available are of value in testing generalisations correlating optical rotatory power and constitution in the sugar group.

As is well known, the late J. U. Nef devoted the closing years of his life to an elaborate study of the condition assumed by sugars in alkaline solution, and it is gratifying to find that additional results are now forthcoming [49] in which the work is extended to the cases of l-arabinose and l-xylose. As was to be expected, these

[44] C. S. Hudson, *J. Amer. Chem. Soc.*, 1918, **40**, 813 ; *A.*, i, 292.

[45] J. B. Cohen and Miss H. S. de Pennington, *T.*, 1918, **113**, 57.

[46] C. S. Hudson and J. K. Dale, *J. Amer. Chem. Soc.*, 1918, **40**, 997 ; *A.*, i, 335.

[47] *Ibid.*, 992 ; *A.*, i, 335.   [48] *Ann. Report*, 1916, 84.

[49] J. U. Nef, O. F. Hedenburg, and J. W. E. Glattfeld, *J. Amer. Chem. Soc.*, 1917, **39**, 1638 ; *A.*, i, 100.

sugars, when oxidised in alkaline solution, give rise to a large variety of oxidation products, and the results not only serve to emphasise the extremely complex nature of a reducing sugar in the alkaline state, but are in agreement with the structural views expressed by Nef in his earlier papers.[50] Nef's ideas also serve to account for the effects which have been observed during the oxidation of maltose in alkaline solution,[51] and, looking back on the publications in which this particular type of sugar oxidation was first discussed, the impression remains that inadequate recognition has been accorded to an extremely fine piece of work. A noteworthy example illustrating the practical application of these ideas is furnished by the successful conversion of rhamnose into methyltetronolactone by the simple process of dissolving the sugar in alkali and passing air through the solution.[52] From the biochemical point of view, the whole question of the oxidation of sugars under mild conditions is important, and signs are not wanting that interest in the subject is being revived.[53]

The interruption of research due to war conditions has delayed the development of systematic work on the specially reactive forms of reducing monosaccharides which are included under the provisional name "γ-sugars," but reference can be made to a paper on the subject which has appeared during the past year.[54] It is now established that in addition to the two crystalline methylgalactosides, a third, non-crystallisable form exists, and it is shown that this variety is analogous in structure to γ-methylglucoside. When completely methylated and the product thereafter hydrolysed, tetramethyl γ-galactose is obtained, and this substance preserves the reactivity which is characteristic of the γ-series. The fact that the methylated sugar undergoes spontaneous autocondensation on keeping, and is thereby converted into an octamethyl γ-digalactose, is a sufficiently striking example of this reactivity to deserve special mention. As a side issue of the research in question, another interesting result emerges. In his original preparation of methylgalactoside, Fischer isolated an amorphous product which he regarded at the time as a third variety of the simple galactoside. It now appears, however, that this substance is a methyldigalactoside, and its formation furnishes another example pointing to the idea that the most ready route to

[50] *Ann. Report*, 1914, 84.

[51] J. W. E. Glattfeld and M. T. Hanke, *J. Amer. Chem. Soc.*, 1918, **40**, 973 ; *A.*, i, 336.

[52] C. S. Hudson and L. H. Chernoff, *ibid.*, 1005 ; *A.*, i, 335.

[53] L. Berczeller and E. Szegö, *Biochem. Zeitsch.*, 1917, **84**, 1 ; *A.*, i, 101

[54] Miss M. Cunningham, *T.*, 1918, **113**, 596.

the synthesis of di- and poly-saccharides is through the γ-form of reducing hexoses.

Another important step has been gained in the identification of γ-sugars in a structural study[55] of the crystalline variety of methyl-fructoside recently isolated by Hudson. This compound is the only known homogeneous methylfructoside, and can thus be converted by standard processes into a tetramethyl fructose which is a definite chemical individual. The compound actually obtained is identical with one of the tetramethyl fructoses previously prepared by Purdie and Paul, and, as a result, it is now possible to construct a scheme illustrative of the complex changes which ensue when fructose is treated with acid methyl alcohol. The ketose, like glucose, behaves both as a butylene oxide and as an ethylene oxide, and thus gives rise to at least four fructosides, two of which are derived from γ-fructose. It is significant that fructose should display this ready tendency to react in the γ-form, particularly as it is the same form which is present in sucrose.

At the same time, it must be recognised that although γ-sugars evidently play an important part in natural processes, other variations of the sugar molecule are often functional. Thus, the prediction made by Fischer some years ago that "glucal" would be found to exist in natural combination is now realised, as the "carbohydrate group" in the nucleic acids has been identified as glucal, and not glucose, as has hitherto been supposed.[56]

So far as synthetic work in the sugar group is concerned, the most outstanding publications of the year deal with the formation of glucose and fructose derivatives in which selected hydroxyl groups are substituted. Details need not be given of the methods employed to limit the substitution to particular positions, as these now present no novel feature, having been standardised in the preparation of partly methylated sugars. The first of the papers[57] refers to the formation of definite mono-, di-, and tetra-benzoyl-glucoses, and of these, the most striking is the monobenzoyl compound, which is apparently identical with the "vacciniin" isolated by Griebel from the whortleberry. The constitution of the new sugar, considering its mode of formation, must be analogous to that of monomethyl glucose,[58] and may thus be regarded as

$$CH_2(OBz) \cdot CH(OH) \cdot CH \cdot [CH \cdot OH]_3 \cdot CH \cdot OH$$

$$O$$

[55] Miss E. S. Steele, *T.*, 1918, **113**, 257.

[56] R. Feulgen, *Zeitsch. physiol. Chem.*, 1917, **100**, 241 ; *A.*, i, 85.

[57] E. Fischer and H. Noth, *Ber.*, 1918, **51**, 321 ; *A.*, i, 225.

[58] J. C. Irvine and T. P. Hogg, *T.*, 1914, **105**, 1386.

The dibenzoylglucose prepared does not seem to have been examined in detail, but in all probability it is likewise represented in nature, as a well-defined dibenzoylglucoxylose has been found in the leaves and stems of *Daviesia latifolia*.

Work on similar lines has been successfully extended to fructose, but it may perhaps be pointed out that the question of structure in these partly substituted hexoses is beset with difficulties, as, in addition to determining the position of the substituting groups, experience has shown that it is necessary to discriminate between the ethylene oxide and butylene oxide types.

The problem of synthesising sugar derivatives comparable with the tannins has again been revived,[59] and here also advantage has been taken of glucose mono- and di-acetones, which have been converted, respectively, into tri- and mono-gallolylglucoses. The trigallolylglucose, however, differs in properties from chebulic acid, and the monogallolyl derivative is not identical with Feist's glucogallic acid. It may be mentioned that, as a preliminary to the work just described, a renewed attempt has been made[60] to obtain *p*-digallic acid with the ultimate object of preparing from it the corresponding chloride for use in the synthesis of tannins. Pentaacetyl-*p*-digallic acid was actually obtained, but, on removing the acetyl groups by carefully regulated hydrolysis, the product proved to be *m*-digallic acid. The transformation thus involved is of general interest, and attention should be directed to it.

Glucosides.—Under this heading, only one paper need be considered. In previous Reports, reference has been made to the thioglucosides prepared from glucose ethyl mercaptal by the action of mercuric chloride, and it now appears that this particular reaction is general,[61] giving rise uniformly to α-thioglucosides. The corresponding β-compounds may, however, be obtained by acting on acetobromoglucose with the potassium salts of mercaptans, and the published description of these compounds leads to the opinion that they are true glucosides containing a five-membered ring in which oxygen is replaced by sulphur.

Disaccharides and Polysaccharides.

Although the publications dealing with di- and poly-saccharides are not numerous, several strikingly important results have to be recorded. Authentic syntheses of disaccharides are few in number, and, excluding those based on the function of enzymes, are charac-

[59] E. Fischer and M. Bergmann, *Ber.*, 1918, 51, 298; *A.*, i, 224.
[60] E. Fischer, M. Bergmann, and W. Lipschitz, *ibid.*, 45; *A.*, i, 172.
[61] W. Schneider, J. Sepp, and O. Stiehler, *ibid.*, 220; *A.*, i, 252.

terised by the use of processes which are drastic and are in no sense parallel to natural synthesis. It is possible, however, to couple reducing hexoses when they are in the form of γ-sugars by comparatively mild agencies to give products which are glucosides of di- and poly-saccharides.[62] To take an example, when galactose or glucose is dissolved in methyl alcohol containing a trace of hydrogen chloride and the solution concentrated, glucoside formation takes place, and simultaneously hexose residues are coupled. so that the ultimate products are respectively methyltetragalactoside and methyltetraglucoside. In this simple way, it is possible to form complexes of high molecular weight, and the ready conversion of maltose into a methyltrimaltoside containing thirty-seven carbon atoms furnishes a striking case in point.

Interest in thio-derivatives of sugars is reviving, and a new departure is marked in a paper describing the synthesis of a definite thio*iso*trehalose. By the action of potassium sulphide on acetobromoglucose, the octa-acetate of a thiodiglucose was obtained. and this was converted into the parent thiodisaccharide by the action of alcoholic ammonia.[63] The corresponding selenium compound has also been obtained, and as both sugars are crystalline, they have been carefully characterised. It is doubtful, however, if these disaccharides are normal in structure in view of their behaviour on hydrolysis and ready capacity to form monopotassium salts, but this does not detract from the inherent interest of the compounds.

Turning to problems of constitution, the important work described last year on the structure of sucrose has been followed by a similar constitutional study of lactose.[64] The method adopted consisted, as usual, of complete methylation, followed by hydrolysis, and the following scheme illustrates the essential steps:

Lactose ⟶ methyl-lactoside ⟶ heptamethyl methyl-lactoside
 ⟶ Tetramethyl hexose (A)
 ⟶ Methyl alcohol
 ⟶ Trimethyl hexose (B)
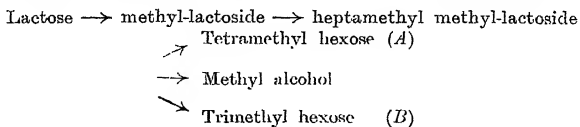
The work thus focussed on the identification of the two methylated hexoses produced and in the allocation of the methyl groups. The product (A) proved to be the butylene oxide form of tetramethyl galactose, whilst the remaining product (B) was recognised as trimethyl glucose, identical with that isolated by Denham from

[62] Miss M. Cunningham, *T.*, 1918, **113**, 604.
[63] F. Wrede, *Biochem. Zeitsch.*, 1917, **83**, 96; *A.*, i, 6.
[64] W. N. Haworth and Miss G. C. Leitch, *T.*, 1918, **113**, 188.

methylated cellulose. The provisional constitution assigned to this methylated glucose is now confirmed, and in consequence the complete structure of lactose may be represented by the following formula :

$$
\begin{array}{ll}
 & \mathrm{CH_2 \cdot OH} \\
\mathrm{-CH\!-\!\!-\!\!-\!\!-O\!-\!\!-\!\!-\!\!-\!\!-\dot{C}H} \\
\ \ \dot{C}H \cdot OH & \ \ \dot{C}H \\
\mathrm{O}\ \dot{C}H \cdot OH & \ \ \dot{C}H \cdot OH \\
\ \ \dot{C}H & \mathrm{O}\ \dot{C}H \cdot OH \\
\ \ \dot{C}H \cdot OH & \ \ \dot{C}H \cdot OH \\
\ \ \dot{C}H_2 \cdot OH
\end{array}
$$

(Galactose residue.)   (Glucose residue.)
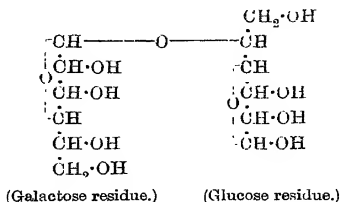
Incidentally, the results have also a direct bearing on the constitution of melibiose, and work of this description goes far to clear up many outstanding problems in the disaccharides. One of the most significant features of the new observations is the experimental evidence pointing to the existence in the case of lactose of what has long been expected, namely, the coupling of hexose residues through secondary alcohol groups. In view of these positive results, it is perhaps superfluous to mention an argument,[65] based on the negative evidence that lactose fails to form an o-tolyl-hydrazone, that the disaccharide is best represented by the un branched chain structure originally assigned to it by Fischer.

Considering current views, it is possible that some workers will be disposed to disagree with the inclusion of cellulose as a subject of discussion under the heading polysaccharides. A few years ago, the idea that cellulose must be regarded as a polyglucose seemed definitely settled by the confident claims made by Willstätter that the complex could be converted quantitatively into glucose. Repetition of this work, under conditions which were certainly no less accurate, has materially weakened the force of Willstätter's argument.[66] It is manifestly impossible to estimate, by means of polarimetric observations, the amount of glucose produced in a system saturated with hydrogen chloride, as this acid produces profound constitutional changes in the sugar. Estimations of reducing power are equally valueless. Some idea of the complexity of the changes involved in the hydrolysis of cellulose is shown by the observation that purified cotton or esparto celluloses, when degraded by mineral acids, are converted into a series of polysaccharide esters. These are capable of forming stable barium salts, and the presence of acidic hydroxyl groups is thus indicated.

[65] A. W. van der Haar, *Rec. trav. chim.*, 1918, 37, 251 ; *A.*, i, 212.

[66] Miss M. Cunningham, *T.*, 1918, 113, 173.

This feature is not characteristic of normal polyglucoses, and the result is disconcerting. In a further paper,[67] by authors whose experience in this subject commands respectful attention, a plea is made for discarding old views and for making a fresh start in elucidating the structure of cellulose. Considering the complexities of the problem, the experimental method based on a study of the products formed on dry distillation under diminished pressure must appear somewhat crude, but the results obtained are not unworthy of attention.[68] Apparently l-glucosan is produced in notable yield, and arising out of this observation, the claim has been made that both starch and cellulose are to be regarded as polymerides of l-glucosan, to which the structure

$$\text{HO·HC}\text{————}\text{CH·OH}$$
$$\text{HC————O————CH}$$
$$\text{H}_2\text{C————O————CH·OH}$$
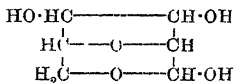
is assigned.[69] The above formula is ingenious, but it does not account for the isolation of the particular form of trimethyl glucose which is obtained from methylated cellulose by hydrolysis.[70]

In a previous Report, reference has been made to investigations on the degradation of starch by means of formaldehyde. This work is being continued, and although a good case may yet be made for the claim that the reactions involved show a striking similarity to those occasioned by diastase, the experimental methods employed seem elementary and do not carry conviction.[71, 72]

Nitrogen Compounds.

Less space than usual need be devoted to the consideration of aliphatic nitrogen compounds, as, judging from the published results, recent work has been conducted on orthodox lines. Some years ago, Meisenheimer gave expression to his views regarding the distribution of the nitrogen valencies in ammonium compounds, and although his opinions were based on the results of specially designed experiments, they were promptly challenged by Fromm. In the interval, little has been heard of the discussion which ensued between these workers, but an authoritative opinion [73] has now

[67] C. F. Cross and E. J. Bevan, *T.*, 1918, **113**, 182.

[68] A. Pictet and J. Sarasin, *Compt. rend.*, 1918, **166**, 38 ; *A.*, i, 59.

[69] J. Sarasin, *Arch. Sci. phys. nat.*, 1918, [iv], **46**, 5 : *A.*, i, 375.

[70] W. S. Denham and Miss H. Woodhouse, *T.*, 1917, **111**, 244.

[71] H. Maggi and G. Woker, *Ber.*, 1918, **51**, 790 ; *A.*, 1, 375.

[72] *Ibid.*, 1917, **50**, 1188 ; *A.*, 1917, i, 686.

[73] S. Komatsu, *Mem. Coll. Sci. Kyōto*, 1918, **3**, 151 ; *A.*, i, 426.

been expressed independently. A review of the properties of known quaternary compounds leads to the conclusion that four of the nitrogen valencies are inter-equivalent, and may be regarded as occupying the apices of a tetrahedron, whilst the fifth principal valency is external, but nevertheless has a fixed position for any individual compound. In one respect, we are thus invited to change our views, but a compromise is possible, as this definite position may vary according to the method whereby the ammonium compound is prepared. This is not improbable, and the adoption of the proposal, which is certainly free from an element of vagueness which characterised Meisenheimer's ideas, accounts satisfactorily for the existence of two distinct forms of *d*-phenylbenzylmethylallylammonium iodide, and also for the isomerism displayed by the semi-ethers derived from trimethylamine oxide.

Amongst numerous new experimental results, mention should be made of a substantial simplification which has been introduced into the preparation of ethylamine and diethylamine through the action of ethyl bromide on alcoholic ammonia.[74] When conducted in the cold, and when the addition of the alkyl bromide is regulated so that the excess of ammonia is maintained at a fixed ratio, practically no tertiary amine is formed. Further, the separation of the primary and secondary amines can be readily effected by taking advantage of the widely different solubilities of the corresponding hydrobromides in chloroform.

Another useful paper[75] devoted to a detailed account of the preparation of dimethylglyoxime is specially noteworthy in view of the public-spirited policy which it reflects. It is the first of a series of publications dealing with the preparation of the less accessible organic compounds, and describing the working methods which have been found most efficient. The scheme will undoubtedly attract much attention, and will be followed by chemists with interest and appreciation.

Catalytic methods for preparing nitriles are now almost bewildering in number. Not only may the dehydration of aldoximes[76] be effected by the use of thorium oxide at 340°, but the same reagent at a higher temperature can bring about the catalytic condensation of aldehydes and ammonia, the change being followed by loss of water, and presumably of hydrogen also.[77] It is doubtful if these methods will prove as generally useful as the corresponding process

[74] E. A. Werner, *T.*, 1918, **113**, 899.

[75] R. Adams and O. Kamm, *J. Amer. Chem. Soc.*, 1918, **40**, 1281 ; *A.*, i, 482.

[76] A. Mailhe and F. de Godon, *Bull. Soc. chim.*, 1918, [iv], **23**, 18 ; *A.*, i, 105.

[77] *Idem, Compt. rend.*, 1918, **166**, 215 ; *A.*, i, 105.

depending on the interaction of an ester and ammonia in presence of aluminium or thorium oxide.[78]

In recent Reports, considerable space has been devoted to the chemistry of carbamides, and although a number of papers on this subject have appeared during the past year, they are concerned chiefly with the continuation of earlier work which has already been fully discussed. More than a passing reference should, however, be made to work which entirely alters our views regarding the constitution of the substances known as *iso*amides or iminohydrins. These compounds, which are prepared by the decomposition of imino-ether hydrochlorides by means of moist silver oxide, were originally regarded as conforming to the type $OH \cdot CR{:}NH$, but this structure was afterwards modified by Hantzsch so as to accommodate the fact that the molecular weights are twice the magnitude demanded by the simple formula. The structure then suggested $(NH{:}CR \cdot O \cdot NH_2{:}CR \cdot OH)$ is also open to criticism, and breaks down when the conductivities of iminohydrins are taken into consideration. As ampholeric electrolytes, these compounds should display low conductivity, whereas the reverse is the case, the results actually obtained being comparable with the values given by a true salt. Then, again, although Hantzsch's formula does not demand that iminohydrins are derivable only from α-hydroxy-acids, this restriction seemed at one time necessary, as all iminohydrins previously known were obtained from this type of acid. Such a view can no longer be held, and all the evidence now available points to the idea that the iminohydrins are in reality amidine salts.[79] The nature of these salts is perhaps not very clear from the general formula $NH_2 \cdot CR{:}NH, R \cdot CO_2H$, and will be best understood by the verbal description that "glycolliminohydrin" is to be regarded as glycollamidine glycollate. The research now under review was initiated by conductivity measurements on the amidine salts, and ended with their synthetical formation on lines conforming to the above structure, and thus furnishes a good example of the searching test which physical methods can bring to bear on problems of structure. From this point of view, it is regrettable that the conductivity of boric acid is but little affected by the addition of compounds containing the group $\cdot NH \cdot CO \cdot$, and thus the application of Böeseken's method of testing constitution is meanwhile excluded from a number of important compounds.[80]

[78] A. Mailhe, *Compt. rend.*, 1918, **166**, 121 ; *A.*, i, 105.

[79] H. G. Rule, *T.*, 1918, **113**, 3.

[80] J. Böeseken [with W. Sturm and G. Goettsch], *Rec. trav. chim.*, 1918, **37**, 144 ; *A.*, ii, 146.

Little progress has been made with research on amino-acids, and no novelties have been noted, but a welcome will be accorded to a useful paper [81] describing the most favourable experimental conditions for preparing typical phosphotungstates. Although these compounds may not be specially suitable for the purpose of identifying amino-acids, they retain a certain value in processes of isolating and purifying individual constituents of mixtures.

Fresh information on the chemistry of proteins is distinctly scanty and unconvincing, the results obtained in the oxidation of the complexes by nitric acid or in the methylation by means of diazomethane being too indefinite to lead to any enlightenment.

The extensive scheme of research on the azides derived from carboxylic acids, to which reference was made last year, has now been brought to a conclusion by the extension of the work to a large number of amino- and substituted amino-acids.[82] As in the earlier papers of the series, the desired compounds have been obtained by well-known processes, and their reactions display no essential novelty, although, concealed within a mass of experimental results, a number of improved working methods may be found.

Very much the same remarks can be applied to the latest paper on the hydrazides and azides of organic acids,[83] and to what is evidently the first of a series of publications on the formation and properties of hydrazino-acids.[84] On the whole, it is evident that, although research on aliphatic nitrogen compounds has been energetically pursued during the past year, a stage has been reached which is characterised by the absence of any noteworthy discoveries.

JAMES COLQUHOUN IRVINE

[81] J. C. Drummond, *Biochem. J.*, 1918, **12**, 5 ; *A.*, i, 336.
[82] T. Curtius, *J. pr. Chem.*, 1917, [ii], **95**, 327 ; *A.*, i, 44.
[83] T. Curtius and O. Hofmann, *ibid.*, **96**. 202 ; *A.*, i, 293.
[84] A. Darapsky, *ibid.*, 251 ; *A.*, i, 506.

PART II. —HOMOCYCLIC DIVISION.

Reactions.

Catalytic Reduction.—The period under review has brought forth a number of papers on reduction with hydrogen gas in the presence of various catalysts. The most important of these describes a general method for the preparation of aldehydes by the reduction of acid chlorides.[1] At the outset, it appeared to be desirable to work at a low temperature with the calculated quantity of hydrogen in order to avoid further reduction to the alcohol, to employ as a solvent ether, which would neither react with the acid chloride nor 'poison' the catalyst, and to neutralise the hydrochloric acid produced in the reaction, by the addition, for instance, of calcium carbonate. Numerous modifications of these conditions only permitted the formation of a trace of benzaldehyde from benzoyl chloride, but eventually a method was discovered by which the reaction could be carried out with nearly the theoretical yield. The conditions were the reverse of those anticipated, hydrogen being passed through a boiling 20 per cent. solution of benzoyl chloride in xylene until the escaping gas no longer contained hydrogen·chloride, indicated by the formation of a cloud with ammonia. Palladinised barium sulphate or Kelber's nickel was employed as catalysts. Benzoyl, butyryl, and stearyl chlorides were thus converted into the corresponding aldehydes, and tricarbomethoxygalloyl chloride into tricarbomethoxygallaldehyde, which gave gallaldehyde on gentle hydrolysis.[2]

There is evidence to show that in reductions by hydrogen gas in the presence of platinum, the presence or absence of oxygen in the catalyst may make a considerable difference to the result. In the reduction of the anhydrides of *o*-dicarboxylic acids, it is found to be necessary to 'prime' the catalyst occasionally by shaking it with air, otherwise the absorption of hydrogen ceases. Employing this method, phthalic anhydride yields as primary products phthalide and *o*-toluic acid, indicating that the five-membered ring is reduced first. Subsequently, hexahydrophthalide, hexahydro-*o*-toluic acid, and hexahydrophthalic acid are produced. In the reduction of phthalimide, however, it is the benzene ring only that suffers reduction, the sole product of the reaction being hexahydrophthalimide.[3]

[1] K. W. Rosenmund, *Ber.*, 1918, **51**, 585 ; *A.*, i, 300.
[2] K. W. Rosenmund and F. Zetzsche, *ibid.*, 594 ; *A.*, i, 300.
[3] R. Willstätter and D. Jaquet, *ibid.*, 767 ; *A.*, i, 391.

D*

An attempt[4] to reduce ω-nitrostyrene to β-nitroethylbenzene in alcoholic or acetic acid solution by hydrogen in the presence of platinum-black was unsuccessful, the product being αδ-dinitro-βγ-diphenylbutane, $NO_2 \cdot CH_2 \cdot CHPh \cdot CHPh \cdot CH_2 \cdot NO_2$. The reduction of ω-nitro-3:4-methylenedioxystyrene gave a similar result.

Furthermore, catalytic reduction has been employed in the preparation of 2:3-dimethoxybenzyl alcohol from o-veratraldehyde,[5] and in the conversion of alcohols, aldehydes, and acids of the terpene group into the corresponding saturated alcohols, aldehydes, and acids.[6]

The removal of halogen from aromatic and other organic compounds by hydrogen in the presence of a catalyst has been the subject of further work[7] designed to render the process more readily applicable to the estimation of halogen in such compounds.

Other papers record the superiority of colloidal palladium over colloidal platinum as a hydrogen carrier,[8] and the anticatalytic influence of mercury and other heavy metals.[9]

The Sulphonation of β-Naphthylamine.[10]—The action of ordinary concentrated sulphuric acid on β-naphthylamine at temperatures below 80° leads to the formation of the 2:8- and 2:5-naphthylaminesulphonic acids in yields of nearly 40 and 60 per cent. of the theoretical respectively, whilst very small proportions of the 2:6- and 2:7-acids are formed as by-products. On prolonged heating at 80° to 120°, however, the 2:8-acid is gradually converted, probably by way of repeated hydrolysis and sulphonation, mainly into the 2:5-acid, and to a small extent into 2:6- and 2:7-acids. At 150—160°, the last two constitute the main product of sulphonation, being probably derived from the 2:6:8- and 2:5:7-disulphonic acids by hydrolysis. The entire mechanism of the sulphonation of β-naphthylamine may probably be represented as follows:

[4] A. Sonn and A. Schellenberg, *Ber.*, 1917, **50**, 1513 ; *A.*, i, 9.
[5] A. Kaufmann and H. Müller, *ibid.*, 1918, **51**, 123 ; *A.*, i, 178.
[6] C. Paal, *D.R.-P.*, 298193 ; *A.*, i, 181.
[7] C. Kelber, *Ber.*, 1917, **50**, 305 ; *A.*, 1917, ii, 215 ; K. W. Rosenmund and F. Zetzsche, *ibid.*, 1918, **51**, 578 ; *A.*, i, 339.
[8] C. Paal and A. Schwarz, *ibid.*, 640 ; *A.*, i, 343.
[9] C. Paal and W. Hartmann, *ibid.*, 711, 894 ; *A.*, ii, 303, 357.
[10] A. G. Green and K. H. Vakil, *T.*, 1918, **113**, 35.
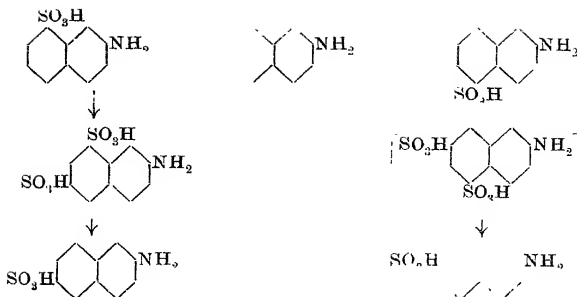
Orientation.

K. J. P. Orton and his co-workers [11] have compared the directing influences of various groups in the chlorination of aromatic compounds by measuring the velocities of reaction, and have established for simple compounds the order $NH_2 > OH > OAlk > NHAc$. W. Fuchs [12] has now arrived at a similar result by examining the products of the bromination of p-aminophenol and its N-acetyl derivative. The former gave 3:5-dibromo-4-aminophenol (I), the ortho-directing influence of the amino-group being greater than that of the hydroxyl group, whilst p-acetylaminophenol gave 2:6-dibromo-4-acetylaminophenol (II), the influence of the hydroxyl group predominating over that of the acetylamino-group.
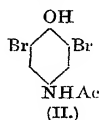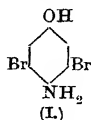
Further communications have appeared on the orientating influence of the alkyloxy-groups in catchol ethers, a subject which was reviewed last year.[13] As the experimental material increases, it becomes more difficult to include all the results in generalisations. J. L. Simonsen and M. G. Rau [14] describe the nitration of 5- and 6-acetylamino-3 : 4-dimethoxybenzoic acids and 4-acetylamino-veratrole.

[11] *Ann. Report*, 1915, 92.
[12] W. Fuchs, *Monatsh.*, 1917, **38**, 331 ; *A.*, i, 64.
[13] *Ann. Report*, 1917, 95.　　　[14] *T.*, 1918, **113**, 22.

5-Acetylamino-3 : 4-dimethoxybenzoic acid (I) yields the 6-nitro-acid (II) in accordance with their views,[15] that the negative

(I.)   (II.)
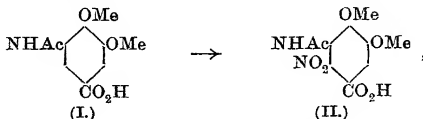
carboxyl group exercises no direct orientating effect except in so far as it neutralises the methoxy-group in the para-position with respect to it, the nitro-group entering the ortho-position with respect to the acetylamino-group and the para-position with respect to the second methoxy-group.

The nitration of 6-acetylamino-3 : 4-dimethoxybenzoic acid (III), however, gave a result that they did not anticipate, the sole product of the reaction being 5-nitro-4-acetylaminoveratrole (IV), which was also obtained from 4-acetylaminoveratrole, whereas they had expected to obtain the 2-nitro-acid (V).

(III.)   (IV.)   (V.)
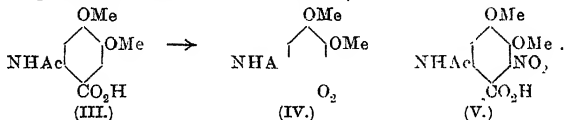
A second paper [16] records that the nitration of 2-methoxy-*m*-tolualdehyde (I) gives a nearly quantitative yield of the 5-nitro-compound (II), whereas the 4-nitro-compound (III) had been

(I.)   (II.)   (III.).
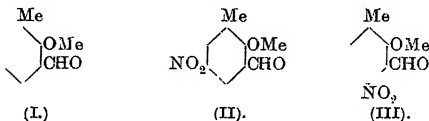
expected in view of the fact that *o*-veratraldehyde (IV) [17] and 5 : 6-methylenedioxy-*o*-tolualdehyde (V) [18] on nitration yield nitro-derivatives containing the nitro-group in the ortho-position with respect to the aldehyde group.

(IV.)   (V.)
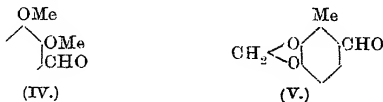
[15] *T.*, 1917, **111**, 224.   [16] J. L. Simonsen, *ibid.*, 1918, **113**, 775.
[17] W. H. Perkin, jun., and R. Robinson, *ibid.*, 1914, **105**, 2389.
[18] W. H. Perkin, jun., *ibid.*, 1916, **109**, 910.

Miss F. Pollecoff and R. Robinson [19] find that the nitration of 5-nitroguaiacol (I) yields mainly 3 : 6-dinitroguaiacol (II) in accordance with the view [20] that negative groups in the meta-position with respect to a positive group exert an influence which is in the direction of favouring ortho-substitution with respect to the positive orientator, but a considerable proportion of the 4 : 5-isomeride (III) is formed at the same time.

HO, MeO NO$_2$ HO MeO NO, NO,   and   HO, MeO NO$_2$ NO$_2$

(I.)   (II.)   (III.)
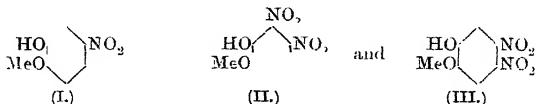
Nitration of 3 : 5-dinitroguaiacol (IV), however, gave a single product, the expected 3 : 5 : 6-trinitroguaiacol (V).

HO MeO NO$_2$ NO$_2$ NO$_2$ HO MeO NO$_2$ NO$_2$

(IV.)   (V.)

The bromination [21] of the two isomeric acetylaminoveratroles and the three acetylaminoveratric acids gave compounds in which the bromine atom entered the para-position with respect to the acetylamino-group in all cases where this position was free. In the case of 6-acetylaminoveratric acid (I), where this position was already occupied, the carboxyl group was eliminated with the formation of 5-bromo-4-acetylaminoveratrole (II).

OMe CO$_2$H OMe NHAc   OMe OMe Br NHAc

(I.)   (II.)

Migration of Acyl Groups.—The crystalline digallic acid obtained by the action of trimethylcarbonatogalloyl chloride on 3 : 5-dimethylcarbonatogallic acid and removal of the methylcarbonato-groups proved unexpectedly to be the meta- and not the para-compound.[22] In an attempt to prepare the missing para-acid, triacetylgalloyl chloride was condensed with 3 : 5-diacetylgallic acid, when penta-acetyl-*p*-digallic acid (I) resulted. On partial

[19] *T.*, 1918, **113**, 645.
[20] T. G. H. Jones and R. Robinson, *ibid.*, 1917, **111**, 903.
[21] J. L. Simonsen and M. G. Rau, *ibid.*, 1918, **113**, 782.
[22] E. Fischer and K. Freudenberg, *Ber.*, 1913, **46**, 1116 ; *A.*, 1913, i, 479.

hydrolysis of this compound, however, the known *m*-digallic acid
(II) was again obtained, which on reacetylation gave penta-acetyl-
m-digallic acid.[23]
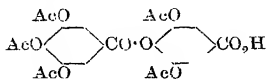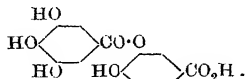
(I.)   (II.)

It thus appeared that migration of the galloyl group had
occurred in the partial hydrolysis of penta-acetyl-*p*-digallic acid, as
in that of pentamethylcarbonato-*p*-digallic acid. The investiga-
tion was then extended to the examination of the behaviour of the
benzoylacetyl derivatives of gallic and protocatechuic acids with
similar results. Thus, methyl 4-benzoyloxy-3-acetoxybenzoate
(III) on partial hydrolysis yields methyl 4-hydroxy-3-benzoyloxy-
benzoate (V), which gives the isomeric methyl 4-acetoxy-3-benzoyl-
oxybenzoate on reacetylation. It is suggested that the methyl
3-hydroxy-4-benzoyloxybenzoate, which is presumably the first
product of the hydrolysis, may possibly pass into the isomeric form
through an intermediate compound, such as that formulated
below (IV).

(III.)   (IV.)   (V.)
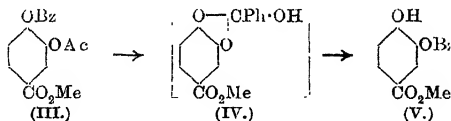
Steric Hindrance.

The study of steric hindrance in tertiary aromatic amines has
given interesting results.

Dimethyl-*o*-toluidine (I) is much less reactive than dimethyl-
aniline towards methyl iodide and in reactions involving substitu-
tion in the para-position with respect to the nitrogen atom, for
example, introduction of the nitroso-group or condensation with
benzaldehyde or formaldehyde. The extension of one of the
N-methyl groups to form a ring, as in 1:8-dimethyl-1:2:3:4-tetra-
hydroquinoline (II), was found previously to be associated with
diminished steric hindrance, and it has now been ascertained[24]

[23] E. Fischer, M. Bergmann, and W. Lipschitz, *Ber.*, 1918, 51, 45 : *A.*, i, 172.
[24] J. von Braun, Z. Arkuszewski, and Z. Köhler, *ibid.*, 282 ; *A.*, i, 257.

that the extension of the *C*-methyl group to form a ring in dimethyltetrahydro-α-naphthylamine (III) gives a similar result.
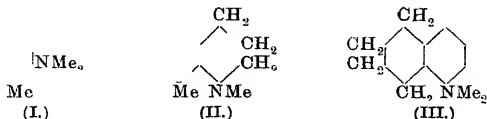
Ring formation is not, however, the principal factor in diminishing the steric hindrance, for dimethyl-*p*-xylidine (IV) is more reactive than dimethyl-*o*-toluidine, and dimethyl-*o*-3-xylidine (V) still more so; dimethyl-*m*-2-xylidine (VI), however, is even less reactive.
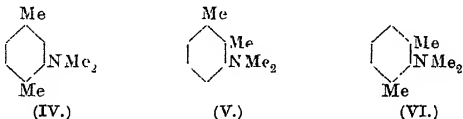
It appears, therefore, that the introduction of a second substituting methyl group neutralises the effect of the first to a large extent when in the ortho-position with respect to it, and to a smaller extent when in the para-position. This behaviour finds an explanation most readily if it is assumed that all the reactions under discussion depend on the preliminary anchoring of the reacting molecule on the nitrogen, and that in dimethyl-*o*-toluidine the residual affinity of the methyl group partly neutralises that of the dimethylamino-group, whereas in the compound (V) above, the second methyl group largely saturates the residual affinity of the first methyl group and allows the residual affinity of the dimethylamino-group to come into play more readily.

A similar attitude towards this problem is adopted by others,[25] who point out the non-reactivity of dimethylaniline oxide in support of their view. The behaviour of methyl *p*-dimethylaminobenzoate and *p*-dimethylaminobenzaldehyde towards nitrous acid is ascribed to the addition of nitrous acid at the nitrogen atom,

$$>NMe_2(OH)\cdot NO,$$ whilst subsequent rearrangement gives in

the case of the ester the substances (I) and (II), and in the case of the aldehyde the compounds (III), (IV), and (V).
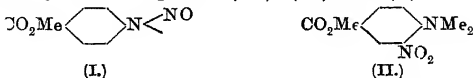
[25] F. Klaus and O. Baudisch, *Ber.*, 1918, **51**, 1036 ; *A.*, i, 430.

$$CHO{<}\quad {>}N{<}^{NO}_{Me}\qquad CHO{<}\quad {>}NMe_2\qquad NO{<}\quad {>}NMe_2$$
$$NO_2$$
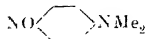
(III.)   (IV.)   (V.)

It was found some years ago[26] that whereas the nitrogen atoms in the compound (I) reacted sluggishly owing to the steric hindrance of the methyl groups in the ortho-position, yet both the nitrogen atoms in the compound (II) were reactive.

$$NMe_2{<}\quad {>}CH_2{<}\quad {>}NMe_2\qquad NMe_2{<}\quad {>}CH_2{<}\quad {>}NMe_2$$
$$Me\qquad\qquad Me\qquad\qquad\qquad\qquad Me$$
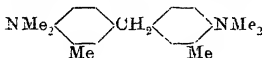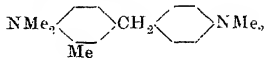
(I.)   (II.)

The lower homologues of these compounds, derived from benzidine instead of diphenylmethane, have now been examined, and it is found[27] that whilst *N*-tetramethyl-*o*-tolidine (III) fails to react with cyanogen bromide and only combines sluggishly with iodoacetonitrile, yet *N*-tetramethyl-*o*-methylbenzidine (IV) readily yields the dicyanamide (V) with the first reagent and gives with iodoacetonitrile a 30 per cent. yield of the dicyanodimethyl derivative (VI).

$$NMe_2{<}\quad {>}-{<}\quad {>}NMe_2\qquad Me_2{<}\quad {>}-{<}\quad {>}NMe_2$$
$$Me\qquad\quad Me\qquad\qquad\qquad\qquad Me$$

(III.)   (IV.)

$$CN{\cdot}NMe{<}\quad {>}-{<}\quad {>}NMe{\cdot}CN$$
$$Me$$

(V.)

$$CN{\cdot}CH_2{\cdot}NMe{<}\quad {>}-{<}\quad {>}NMe{\cdot}CH_2{\cdot}CN$$
$$Me$$
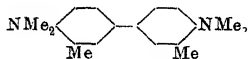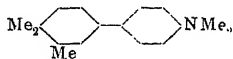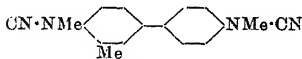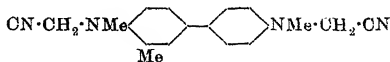
(VI.)

To steric influence is attributed the abnormal behaviour of *iso*valeric acid in the Perkin synthesis.[28] Benzaldehyde, *iso*valeric anhydride, and sodium *iso*valerate yield ten times as much of the hydrocarbon (I) as of the unsaturated acid (II) at 100°

$$CHPh{:}CH{\cdot}CHMe_2\qquad CHPh{:}C(CO_2H){\cdot}CHMe_2$$
(I.)   (II.)
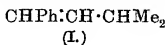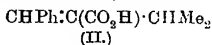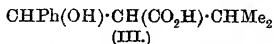
$$CHPh(OH){\cdot}CH(CO_2H){\cdot}CHMe_2$$
(III.)

[26] J. von Braun and O. Kruber, *Ber.*, 1913, **46**, 3470 ; *A.*, 1913, i, 1333.

[27] J. von Braun and M. Mintz, *ibid.*, 1917, **50**, 1651 ; *A.*, i, 127.

[28] A. Schaarschmidt, E. Georgeacopol and J. Herzenberg, *ibid.*, 1918, **51**, 1059 ; *A.*, i, 431.

The hydrocarbon does not appear to be formed directly from the acid, for this is stable at 100°, and it is suggested that the hypothetical primary product of the reaction, the hydroxy-acid, (III), first suffers the loss of carbon dioxide owing to the proximity of the *iso*propyl group, and then yields the hydrocarbon by dehydration.

Colour and Constitution.

Chromoisomerism.—P. Pfeiffer has continued his investigation of the occurrence of certain nitromethoxystilbenes in two forms of different colour, termed cryptoisomerides.[29] His latest paper deals with the conditions which must be fulfilled in order that nitrostilbenes may be capable of exhibiting cryptoisomerism. 4-Nitro-4′-methoxystilbene (I) exists in two varieties of different colour, and so also does 4-nitro-2-cyano-4′-methoxystilbene. Introduction of the cyano-group into the 3-position, however, gives rise to a compound which occurs in one form only. 2-Nitro-4-cyano-4′-methoxystilbene (II) and the corresponding carboxylic acid, its salts and esters, each occurs in two forms, but 2-nitro-4-cyano-2′(and 3′)-methoxystilbenes only exist in one form. 2-Nitro-4-acetylamino(and 4-benzoylamino)-4′-methoxystilbenes also exist in two forms, so that the phenomenon is characteristic of 2- and 4-nitro-4′-methoxystilbenes.

$$NO_2 \underset{(I.)}{\diagup \diagdown} CH:CH \diagup \diagdown OMe \qquad CN \diagup \diagdown CH:CH \underset{\underset{(II.)}{NO_2}}{\diagup \diagdown} OMe \ .$$
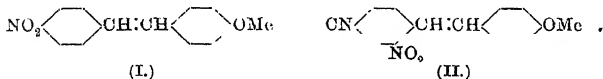
After this examination of the influence of the positions of the above groups, Pfeiffer deals with the effect of substituting other groups for the methoxyl group of 4-nitro-2-cyano-4′-methoxystilbene, and finds that its replacement by hydrogen or by alkyl groups gives substances occurring only in one form. Its substitution by hydroxyl, however, gives a substance occurring in two varieties, but the acyl derivatives of this compound occur in one form only. These results lead him to the view that nitrostilbenes only occur in chromoisomeric forms when, besides the chromophoric groups (the nitro-group and ethylene linking), an auxochromic group is also present. Attention is also directed to the fact that, of the two varieties, the paler coloured is similar in colour to the corresponding compound lacking the auxochromic group, whilst in the deeper coloured variety the typical auxochromic action comes into play.

[29] *Ann. Report*, 1916, 108 ; 1917, 102 ; *Ber.*, 1918, **51**, 554 ; *A.*, i, 344.

Fluorescence.—The fluorescence of platinocyanides indicates that the cyano-group has a favourable influence on this phenomenon, and it is known that even such a simple compound as benzonitrile is fluorescent in the ultra-violet. Like the platinocyanides, many organic cyanogen compounds are only fluorescent in the solid state, for example, the compound $CPh(CN){:}CH{\cdot}C_6H_4{\cdot}NMe_2$. Since *N*-methyl groups often inhibit fluorescence, the corresponding primary amine, $CPh(CN){:}CH{\cdot}C_6H_4{\cdot}NH_2$, was also examined, but proved to be less fluorescent in the solid state and devoid of this property in solution.

The isomeride of this compound, $CHPh{:}C(CN){\cdot}C_6H_4{\cdot}NH_2$, however, showed a strong fluorescence both in the solid state and in solution, the contrast indicating the effect of constitutional changes on fluorescence. A further number of somewhat disconnected instances of the relation between chemical constitution and fluorescence are given in the same paper.[30]

Synthesis of naturally occurring Compounds.

The earlier syntheses of tropic acid, a hydrolytic product of both atropine and hyoscine, are too cumbrous to serve as methods for its preparation, but a simple and effective synthesis has now been discovered. It is well known that ethyl phenylacetate can be condensed with ethyl formate in the presence of sodium, yielding a mixture of desmotropic ethyl formylphenylacetates. On reducing this product with aluminium amalgam in ethereal solution, ethyl tropate results.[31] The reaction has been carried out independently with the methyl esters.[32]

$$CH_2Ph{\cdot}CO_2Et \longrightarrow CPh({:}CH{\cdot}OH){\cdot}CO_2Et \longrightarrow$$
$$CHPh(CH_2{\cdot}OH){\cdot}CO_2Et.$$
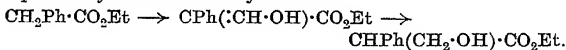
Elemicin, $3:4:5$-trimethoxyallylbenzene, a constituent of the volatile oil of elemi, has been synthesised by the following method.[33] The condensation of allyl bromide and pyrogallol $2:6$-dimethyl ether yields $2:6$-dimethoxyphenyl allyl ether (I). This is con-
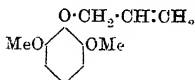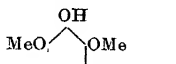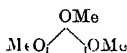
(I.)   (II.)   (III.)

[30] H. Kauffmann, *Ber.*, 1917, **50**, 1614; *A.*, i, 113.

[31] E. Müller, *ibid.*, 1918, **51**, 252; *A.*, i, 223; Chemische Werke Grenzach, *D.R.-P.*, 302737; *A.*, i, 300.

[32] W. Wislicenus and E. A. Bilhuber, *ibid.*, 1237; *A.*, 1919, i, 19.

[33] F. Mauthner, *Annalen*, 1917, **414**, 250; *A.*, i, 428.

verted by heating for a few minutes at 220° into 2:6-dimethoxy-4-allylphenol (II), which yields elemicin (III) on methylation.

The position of the allyl group in the synthetic compound has been determined by oxidation, when gallic acid trimethyl ether is obtained.

Curcumin, the colouring matter of turmeric, is a substituted derivative of dicinnamoylmethane, and has the formula given below:
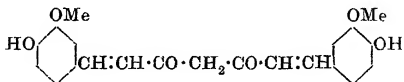
It has been synthesised recently by an application of the method employed previously for the synthesis of dicinnamoylmethane.[34] In this, cinnamoyl chloride was condensed with ethyl acetoacetate and the product hydrolysed, when cinnamoylacetone resulted. Condensation of this product with a second molecule of cinnamoyl chloride and hydrolysis of the product gave dicinnamoylmethane.

$$CHPh:CH \cdot COCl \longrightarrow CHPh:CH \cdot CO \cdot CHAc \cdot CO_2Et \longrightarrow$$
$$CHPh:CH \cdot CO \cdot CH_2Ac \longrightarrow (CHPh:CH \cdot CO)_2CHAc \longrightarrow$$
$$(CHPh:CH \cdot CO)_2CH_2.$$
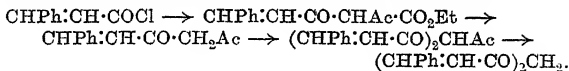
By employing carbomethoxyferuloyl chloride (I) in the place of cinnamoyl chloride, the dicarbomethoxy-derivative of curcumin was obtained. It gave curcumin on hydrolysis.[35]
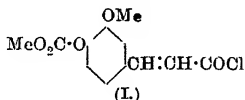
By analogous methods, p-hydroxy- and pp'-dihydroxy-cinnamoyl-methanes have been prepared.[36]

A new synthesis of adrenaline has been described.[37] Diacetyl-protocatechualdehyde (I), on condensation with nitromethane in feebly alkaline aqueous solution, yields β-hydroxy-β-3:4-diacetoxy-
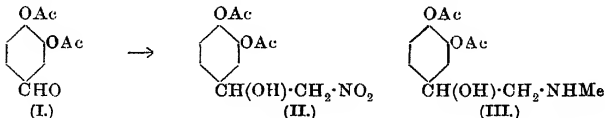
[34] V. Lampe and T. Milobendzki, *Ber.*, 1913, **46**, 2235; *A.*, 1913, i, 876.
[35] V. Lampe, *ibid.*, 1918, **51**, 1347; *A.*, 1919, i, 30.
[36] V. Lampe and M. Godlewska, *ibid.*, 1355; *A.*, 1919, i, 31.
[37] N. Nagai, *Jap. Pats.*, 32440, 32441, 1918.

phenylnitroethane (II). When this is mixed with the calculated quantity of formaldehyde and reduced by means of zinc and acetic acid, β-hydroxy-β-3 : 4-diacetoxyphenylethylmethylamine (III) is formed, from which adrenaline is obtained on removal of the acetyl groups.

Ethylene Oxides.

The preparation of many more complex ethylene oxides [38] by the action of sodium ethoxide on ω-halogenoacetophenones in the presence of aromatic aldehydes has been effected.

Benzaldehyde has been successfully condensed with several ω-halogenoacetophenones containing positive substituents

$$(CH_3, OMe, NHAc),$$
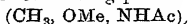
but no crystalline compounds were obtained when ω-bromo-m-nitro-acetophenone or ω-chloro-5-nitro-4-acetylaminoacetophenone were employed.[39]

On the other hand, ω-bromoacetophenone has been subjected to the action of sodium ethoxide in the presence of a large number of aldehydes, and found to yield ethylene oxides readily with those containing negative substituents (NO_2, Cl, etc.), whereas no such condensation took place with aliphatic aldehydes or with certain aromatic aldehydes containing only positive substituents, such as anisaldehyde and p-tolualdehyde.[40]

It is suggested that the formation of ethylene oxides in this reaction takes place according to the scheme:

$$PhCO \cdot CH_2Br + PhCHO \longrightarrow PhCO \cdot CHBr \cdot CH(OH)Ph \longrightarrow$$
$$PhCO \cdot CH {\displaystyle \mathop{<}^{CHPh}_{O}}$$
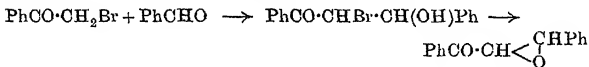
and is thus analogous to the condensation of acetophenone with aldehydes, where in certain cases ketonic alcohols have been isolated as intermediate products.

$$PhCO \cdot CH_3 + R \cdot CHO \longrightarrow PhCO \cdot CH_2 \cdot CH(OH)R \longrightarrow$$
$$PhCO \cdot CH {:} CHR.$$
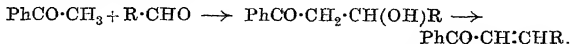
The tendency of simple ethylene oxides to yield the corresponding ketones on heating alone or with catalysts,

$$\underset{\diagdown \diagup}{-CH \cdot CH-} \quad - \quad -CH_2 \cdot CO-$$
$$O$$

is not shared by the complex ethylene oxides under discussion, but

[38] Compare *Ann. Report*, 1917, 105.
[39] H. Jörlander, *Ber.*, 1917, **50**, 1457 ; *A.*, i, 20.
[40] S. Bodforss, *ibid.*, 1918, **51**, 192 ; *A.*, i, 229.

change of this type can be brought about by exposure of the substance in methyl-alcoholic solution, to ultra-violet light, benzoylphenylethylene oxide, for instance, yielding phenyl α-hydroxystyryl ketone.[41]

$$PhCO \cdot CH \underset{O}{\overset{CHPh}{<}} \qquad\qquad PhCO \cdot C(OH) : CHPh .$$

Polycyclic Aromatic Hydrocarbons.

Indenes.– Some years ago, C. Courtot[42] showed that Thiele's theory of the oscillation of the double linking in the indene nucleus was incorrect by isolating both 1- and 3-substituted indenes, for example, 1- and 3-benzylindene. Thiele and his pupils[43] have arrived at the same result by a slightly different method. Indene (I) is condensed with an aldehyde, R·CHO, and the product (II) is reduced, the resulting compound (III) being condensed with a second aldehyde, R′·CHO, when the compound (IV) is obtained.

(I.)   (II.)   (III.)

(V.)   (X.)   (IV.)
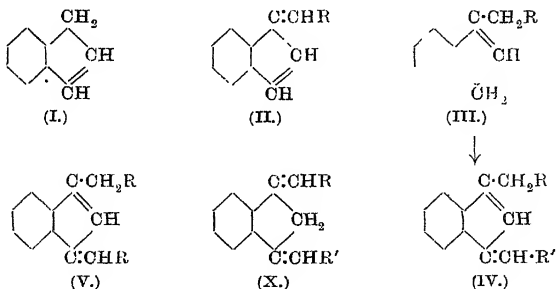
By conducting the same operations, but changing the order of the addition of the aldehydes, the isomeric compound (V) is formed. Several pairs of isomerides have been prepared from aromatic aldehydes by this method.

The stability of the two forms depends on the balance of the residual affinities of the groups R and R′. To take an extreme case, where R is aromatic and R′ is hydrogen, compounds of the

[41] S. Bodforss, *Ber,* 1918, **51**, 214 ; *A.,* i, 232.

[42] *Ann. Report,* 1915, 117.

[43] J. Thiele and K. Merck, *Annalen,* 1918, **415**, 257 ; W. Bernthsen, *ibid.,* 274 ; H. M. Wüest, *ibid.,* 291 ; *A.,* i, 484, 486, 488.

type (VI) cannot be isolated owing to the readiness with which they pass to the isomeric form (VII).

$$C{:}CH_2R$$
$$CH$$
$$C{:}CH_2$$
(VI.)

$$C{:}CHR$$
$$CH$$
$$C{\cdot}CH_2$$
(VII.)
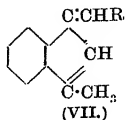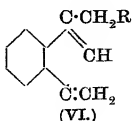
Where both the groups R and R' are aromatic, the two varieties can usually be isolated, but may differ in stability. Thus, 1-benzylidene-3-p-methoxybenzylindene (VIII) is isomerised to 1-anisylidene-3-benzylindene (IX) when boiled with alkali.

$$C{:}CHPh$$
$$CH$$
$$C{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe$$
(VIII.)

$$C{:}CH{\cdot}C_6H_4{\cdot}OMe$$
$$CH$$
$$C{\cdot}CH_2Ph$$
(IX.)
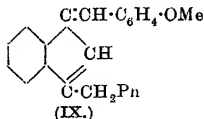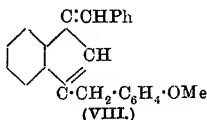
In some cases, however, both forms are stable towards boiling alkali, for instance, when R and R' are phenyl and 2:4-dichlorophenyl respectively; in others, the action of alkali brings about an equilibrium between the two forms, for instance, when R and R' are phenyl and p-tolyl.

It is interesting to note that in two cases (where R = furyl, and R' = phenyl, or p-methoxyphenyl) it has been possible to isolate the intermediate product (X) as well as the extreme forms (IV) and (V).

Anthraquinones.—J. L. Simonsen[44] has thrown more light on the constitution of the natural colouring matter, morindone, which was known to yield 2-methylanthracene on distillation with zinc dust, and believed to be a trihydroxymethylanthraquinone.[45] This view has now been confirmed, and it is found, further, that two of the hydroxy-groups must be in the ortho-position with respect to the carbonyl groups of the anthraquinone nucleus, since treatment with methyl iodide and alkali only yielded a monomethyl ether, whilst two of the hydroxyl groups are probably in the 1:2-position, since morindone is a mordant dye resembling alizarin. These and other reasons lead to the belief that it has one of the two formulæ given, (I) being thought the more probable.

44 *T.*, 1918, **113**, 766.
45 A. G. Perkin and J. J. Hummel, *ibid.*, 1894, **65**, 851.

(I.)   (II.)
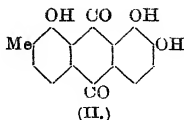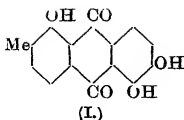
The oxidation of alizarin (III) by potassium ferricyanide in alkaline solution is found to yield an acid having the probable formula (IV).[46]

(III.)   (IV.)
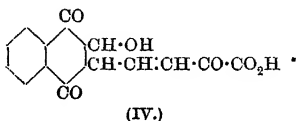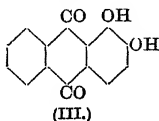
Benzanthrone.—It has been shown previously that 1-phenyl-naphthalene-2 : 3-dicarboxylic anhydride (I) can be converted into the isomeric 3 : 4-benzofluorenone-1-carboxylic acid (III) by the prolonged action of cold concentrated sulphuric acid or by means of aluminium chloride in benzene. The change can also be brought about by alkaline hydrolysis to the dicarboxylic acid (II) and subsequent treatment with cold sulphuric acid.

(I.)   (II.)   (III.)
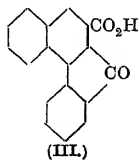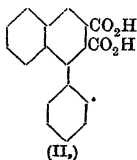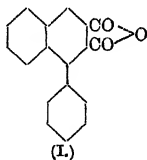
In an attempt[47] to hasten the formation of the end-product by varying the conditions of the first-mentioned method of preparation, 1-phenylnaphthalene-2 : 3-dicarboxylic anhydride was heated with concentrated sulphuric acid for three hours at 155°, when benzanthronecarboxylic acid (V) was formed, together with a sulphonic acid, probably derived from 3 : 4-benzofluorenone-1-carboxylic acid. The reaction is an instance of intramolecular change of a five-membered ring to the more stable six-membered ring.

Benzanthronecarboxylic acid was prepared previously by the fusion of the compound (III) with potassium hydroxide, yielding

[46] R. Scholl and A. Zinke, *Ber.*, 1918, **51**, 1419 ; *A.*, 1919, i, 25.
[47] A. Schaarschmidt and E. Korten, *ibid.*, 1074 ; *A.*, i, 433.

the acid (IV), and treatment of this with cold concentrated sulphuric acid.

(III.)

(IV.)

(V.)
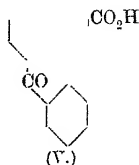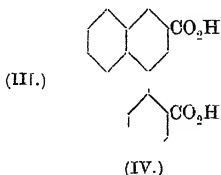
Whilst the acid (IV) is the sole product of the fusion of the anhydride (III) with alkali hydroxide, the parent compound, 3 : 4-benzofluorenone (VI), yields the salts of both 1-phenyl-naphthalene-2-carboxylic acid (VII) and o-α-naphthylbenzoic acid (VIII) under this treatment.[48]

(VI.)   and   (VII.)   (VIII.)
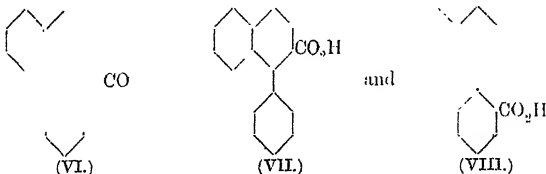
Dehydrogenation.—The dehydrogenation of acenaphthene with the formation of decacyclene and fluorocyclene, which was con-

$$C_{10}H_6 \begin{matrix} CH_2 \\ \end{matrix} \qquad C_{10}H_6 \begin{matrix} C \cdot \\ C \cdot \end{matrix}_2 \quad \text{and} \quad C_{10}H_6 \begin{matrix} CH \cdot \\ C \vdots \end{matrix}$$
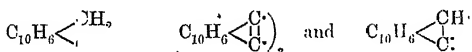
ducted previously by heating at 280—290°, can be effected more conveniently by heating a mixture of the compound with litharge to 300—380° in a sealed tube.[49] From the by-products of the reaction, a green hydrocarbon, $C_{48}H_{20}$, termed chlorene, has been isolated. The method may prove to be of use in the dehydrogenation of other hydrocarbons.

[48] A. Schaarschmidt and E. Georgeacopol, *Ber.*, 1918, 51, 1082 ; *A.*, i, 434.
[49] K. Dziewoński and S. Suknarowski, *ibid.*, 45 7 ; *A.*, i, 296.

Hydrocyclic Compounds and Terpenes.

Derivatives of cycloPropane.—A new mode of preparation of *cyclo*propane derivatives has been discovered in the action of ω-halogenoacetophenones on certain 3-substituted coumarins in the presence of sodium ethoxide.[50]

$$C_6H_4 {<}^{CH:CR}_{O---CO} \ + \ CH_2Br\cdot COPh \qquad C_6H_4 {<}^{\overset{CH\cdot COPh}{\overset{|}{CH\cdot CR}}}_{O-\ -CO}.$$
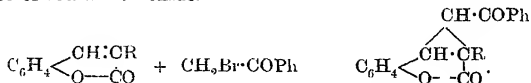
In this reaction, the substituent in the 3-position of the coumarin nucleus may be an acyl (acetyl, propionyl, or benzoyl), a carboxyalkyl, or the cyano-group. The constitution of the condensation product is proved in the case of 3-carbethoxycoumarin (I) by hydrolysis, when a dibasic acid (II) is produced, together with salicylaldehyde (III) and phenacylmalonic acid (IV).

$$C_6H_4 {<}^{\overset{CH\cdot COPh}{\overset{\triangle}{CH\cdot \overset{|}{C}\cdot CO_2Et}}}_{O---CO} \qquad C_6H_4 {<}^{CH(OH)\cdot \overset{CH_2\cdot COPh}{\overset{|}{\underset{CO_2H}{C}\cdot CO_2H}}}_{OH}$$

$$\text{(I.)} \qquad\qquad\qquad \text{(II.)}$$

$$C_6H_4 {<}^{CHO}_{OH} \quad \text{and} \quad PhCO\cdot CH_2\cdot CH(CO_2H)_2.$$

$$\text{(III.)} \qquad\qquad \text{(IV.)}$$
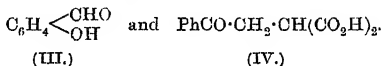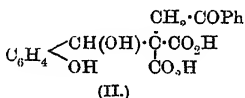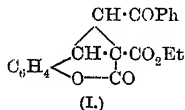
The formation of *cyclo*propane derivatives does not take place when the 3-substituent, R, is hydrogen or the phenyl group, or with 4-carbethoxycoumarin. It thus appears to be confined to coumarins containing the groups of acetoacetic, malonic, and cyanoacetic esters. The reaction has been carried out successfully with several aryl halogenomethyl ketones, but cannot be effected with chloroacetone.

Derivatives of cycloHexanone.—The influence of the position of the bromine atoms in a number of dibrominated *cyclo*hexanones on the behaviour towards aqueous potassium hydroxide has been studied with interesting results.[51] In the case of compounds formed by the saturation by bromine of an ethylene linking adjacent to the carbonyl group, different results are obtained according as the carbon atom next to the carbonyl group is attached to

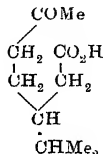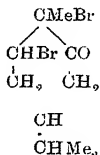[50] O. Widman, *Ber.*, 1918, **51**, 533, 907, 1210; *A.*, 1918, i, 347, 393; 1919, i, 32.

[51] O. Wallach, *Annalen*, 1918, **414**, 271; *A.*, i, 440.

hydrogen or to an alkyl group. In the first case, phenols are formed; thus, carvacrol from 3 : 4-dibromocarvomenthone.

CHMe
$$CH_2 \; CO$$
$$CH_2 \; CHBr$$
$$CBr$$
$$CHMe_2$$

Me
OH
$$CHMe_2$$
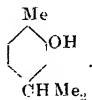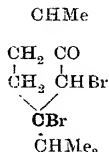
In the second, fission of the ring takes place, with the formation of aliphatic ketonic acids containing the same number of carbon atoms; thus, 1 : dibromocarvomenthone yields ε-keto-β-*iso*propyl-heptoic acid.

CMeBr
$$CHBr \; CO$$
$$CH_2 \quad CH_2$$
CH
$$CHMe_2$$

COMe
$$CH_2 \; CO_2H$$
$$CH_2 \; CH_2$$
CH
$$CHMe_2$$

Where the bromine atoms are divided between the nucleus and the side-chain, or are both in the side-chain, the results are so various that no generalisation can be made. The most valuable results, however, are obtained when the bromine atoms are attached to the two carbon atoms adjacent to the carbonyl group, when pentacyclic α-hydroxycarboxylic acids result.[52]

In connexion with the elimination of halogen hydrides from derivatives of terpenes, another investigation may be noted. Whilst all the alkaline reagents previously employed for the removal of hydrogen chloride from nitrosochlorides have disadvantages, it has now been found that pyridine in acetone solution gives excellent results.[53]

The Wagner Rearrangement.—The conversion of borneol (I)— a substance of the camphor type—into camphene (II)—a substance of the fenchone type—on dehydration, and the reverse change from the fenchone to the camphor type in the dehydration of fenchyl alcohol (III) to α-fenchene (IV), has been explained hitherto in two ways by the assumption of the intermediate form-

[52] O. Wallach, *Annalen*, 1918, **414**, 296 ; *A.*, i, 442. Compare *Ann. Report*, 1916, 116.

[53] O. Wallach, *ibid.*, 257 ; *A.*, i, 439.

ation on the one hand of a tricyclene, and on the other of a sub-stance containing a bivalent carbon atom. The formulæ of the
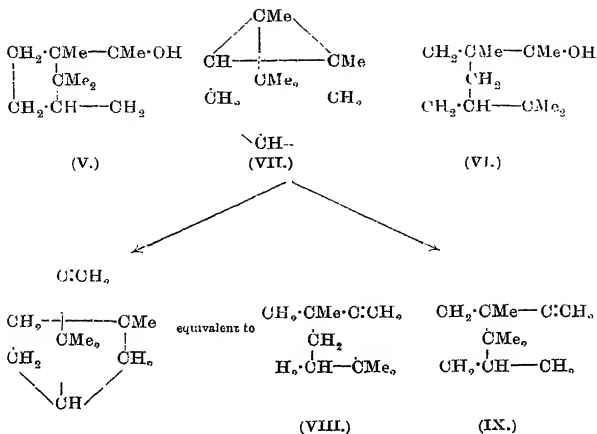
$$CH_2 \cdot CMe \text{---} CH \cdot OH$$
$$| \qquad | \qquad$$
$$\qquad CMe_2$$
$$| \qquad |$$
$$CH_2 \cdot CH \text{----} CH_2$$
(L.)

$$CH_2 \cdot CH \text{---} C\!:\!CH_2$$
$$| \qquad | \qquad |$$
$$\qquad CH_2 \qquad |$$
$$| \qquad | \qquad |$$
$$CH_2 \cdot CH \text{---} CMe_2$$
(II.)

$$CH_2 \cdot CMe \text{---} CH \cdot OH$$
$$| \qquad |$$
$$\qquad CH_2$$
$$| \qquad |$$
$$CH_2 \cdot CH \text{----} CMe_2$$
(III.)

$$CH_2 \cdot CH \text{---} C\!:\!CH_2$$
$$| \qquad |$$
$$\qquad CMe_2$$
$$| \qquad |$$
$$CH_2 \cdot CH \text{---} CH_2$$
(IV.)
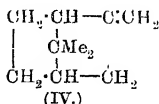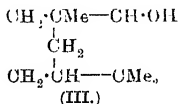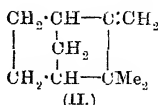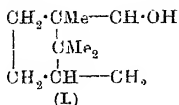
alternative hypothetical intermediate products resulting from the dehydration of borneol are as follows :

$$CH \text{-}|\text{----}CH$$

$$CH_2 | \qquad OH$$

$$\diagdown CH \text{-} \diagup$$
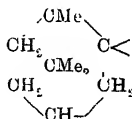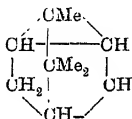
From the first, camphene would result by fission of the marked linking of the trimethylene ring, whilst in the case of the second formula, rearrangement of the linkings would be necessary for the change.

Whilst in the case of secondary alcohols, such as borneol, the two explanations are possible, the occurrence of the Wagner re-arrangement in the dehydration of a tertiary alcohol could only be explained by the first assumption. It has now been found[54] that the tertiary alcohols methylborneol (V) and methylfenchyl alcohol (VI) both undergo this rearrangement to some extent on dehydration, yielding the same mixture of hydrocarbons, from which both camphor and fenchone are obtained on ozonisation. This result can be explained by the assumption that both alcohols yield as an intermediate product the tricyclene (VII), the tri-methylene ring of which ruptures in two of the three possible ways to yield a mixture of methylcamphene (VIII) and methyl-α-fenchene (IX).

[54] L. Ruzička, *Helv. Chim. Acta*, 1918, **1**, 110 ; *A.*, i, 398. Compare *Ann. Report*, 1914, 119.

$$CH_2 \cdot CMe - CMe \cdot OH$$
$$| \quad CMe_2$$
$$CH_2 \cdot CH - CH_2$$

(V.)

$$CMe$$
$$CH - | - CMe$$
$$CMe_2$$
$$CH_2 \qquad CH_2$$
$$CH -$$

(VII.)

$$CH_2 \cdot CMe - CMe \cdot OH$$
$$| \quad CH_2$$
$$CH_2 \cdot CH - CMe_2$$

(VI.)

$$C:CH_2$$
$$CH_2 - | - CMe$$
$$CMe_2 \quad |$$
$$CH_2 \qquad CH_2$$
$$CH$$

equivalent to

$$CH_2 \cdot CMe \cdot C:CH_2$$
$$CH_2$$
$$H_2 \cdot CH - CMe_2$$

(VIII.)

$$CH_2 \cdot CMe - C:CH_2$$
$$CMe_2$$
$$CH_2 \cdot CH - CH_2$$

(IX.)

Spinacene.—The liver oil of certain fishes belonging to the Spinacidæ or Squalidæ, a family of sharks, contains about 90 per cent. of an unsaturated liquid hydrocarbon. This compound, termed spinacene by A. C. Chapman,[55] has the formula $C_{29}H_{48}$ and forms compounds with both three and six molecular proportions of hydrogen chloride and nitrosyl chloride. It appears to be related to the terpenes, and yields a compound, $C_{10}H_{18}$, probably a *cyclo*dihydroterpene, when distilled over sodium under 45 mm. pressure.

Aromatic Compounds of Nitrogen.

Coupling.—The mechanism of diazo-coupling continues to arouse discussion. An account of the views of K. H. Meyer, K. von Auwers, and P. Karrer was given in a previous Report.[56]

One of the arguments brought forward by the last author in support of his view that the addition of diazo-salts to amines takes place at the nitrogen atom, was the supposed inability of di-*n*-butyl- and di*iso*amyl-aniline to couple without the loss of an alkyl group.

[55] *T.*, 1917, **111**, 56; 1918, **113**, 458. Compare M. Tsujimoto, *J. Ind. Eng. Chem.*, 1916, **8**, 889; 1917, **9**, 1098; *A.*, 1916, i, 786; 1918, i, 89.

[56] *Ann. Report*, 1915, 115.

In so far as di-n-butylaniline is concerned, the experimental basis of the work appears to be faulty, for J. Reilly and W. J. Hickinbottom[57] have now shown that di-n-butylaniline combines in quite a normal manner with diazotised sulphanilic acid, yielding 4-di-n-butylaminoazobenzene-4'-sulphonic acid,

$$(C_4H_9)_2N \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot SO_3H.$$
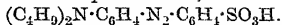
O. Dimroth and collaborators[58] have investigated the question raised by von Auwers as to whether the O-azo-compounds obtainable from phenols and certain enolic compounds are truly O-azoethers, $R \cdot N \colon N \cdot OR'$, or diazonium salts, $R \cdot N(\colon N) \cdot O \cdot R'$. For this purpose, they have measured the electrical conductivity of several members of the class obtained by the action of 4-benzoylaminonaphthalene-1-diazonium chloride or p-acetylaminobenzenediazonium chloride on phenols of different degrees of acidity, and find that the conductivity of the compounds of the first-mentioned salt with picric acid ($\mu = 30 \cdot 48$) and dinitrophenol ($\mu = 22 \cdot 0$) is of the same order as that of the chloride ($\mu = 31 \cdot 37$) in aqueous acetone. These compounds, therefore, react as diazonium salts in solution. On the other hand, the conductivity of the compounds with acetyldibenzoylmethane ($\mu = 0 \cdot 26$) and pentamethylphenol ($\mu = 0 \cdot 41$) is comparable with that of p-nitrobenzenediazomethyl ether ($\mu = 0 \cdot 79$), which is doubtless a true O-azo-ether.

All the compounds prepared, however, whether from phenols of strongly or feebly acidic properties or from aliphatic enols, suffer fission on treatment with ethereal hydrogen chloride, yielding the diazonium chloride and the original hydroxylic constituent. Moreover, they couple with phenols and amines. Both reactions—fission and coupling—take place less readily in the case of the derivatives of aliphatic enols.

Attention may be directed here to a consideration of this problem based on the theory of addition of partly dissociated complexes, to which brief reference was made last year.[59]

Diazoimines.—Following on the preparation of acyl-p-phenylenediazoimides by diazotising acyl-p-phenylenediamines with liquid nitrous anhydrides in dry acetone,[60] the formation of some unstable free diazoimines by the same method is recorded. Nitro-p-phenylenediamine (I) yields the diazoimine (II), which, although itself unstable except in a freezing mixture, is converted into the
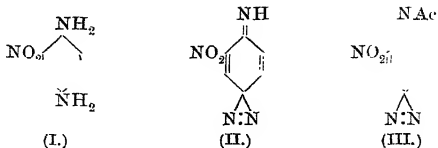
[57] *T.*, 1918, **113**, 99.

[58] O. Dimroth, H. Leichtlin, and O. Friedemann, *Ber.*, 1917, **50**, 1534; *A.*, i, 128.

[59] Mrs. G. M. Robinson and R. Robinson, *T.*, 1917, **111**, 963; *Ann. Report*, 1917, 134.
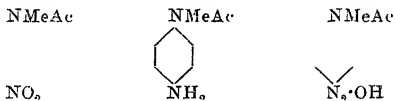
[60] *Ann. Report*, 1917, 115.

stable 3-nitro-4-acetyl-*p*-phenylene-1-diazo-4-imide (III) on acetyl-ation.

Similar results were obtained with 2 : 6-dichloro-*p*-phenylene-diamine.[61]

Formyl- (and acetyl)- methylaminobenzene-4-diazohydroxides can be obtained from the corresponding methylacylanilines by nitra-tion, reduction, and treatment with nitrous anhydride in dry acetone.[62]

Bromoalkylated Aromatic Amines.—When methylaniline and ethylene dibromide are heated at 100° in the proportion of four molecules to one, the main reaction is the formation of diphenyl-dimethylethylenediamine,

$$4\text{PhNHMe} + \text{CH}_2\text{Br·CH}_2\text{Br} = \text{PhNMe·CH}_2\text{·CH}_2\text{·NMePh} + 2\text{PhNHMe,HBr},$$
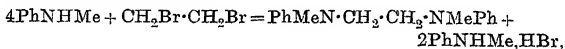
but even under these conditions a trace of methyl-β-bromoethyl-aniline, NPhMe·CH$_2$·CH$_2$Br, is formed, whilst the yield of this compound can be increased to 35 per cent. by employing a larger proportion of ethylene dibromide in the condensation.[63]   Methyl-β-bromoethylaniline is a very reactive compound, and can be sub-jected successfully to all the reactions characteristic of tertiary aromatic amines and aliphatic bromo-compounds.

Several compounds of a similar type have been prepared and their reactions studied.   For the most part, these are without any special importance, but one is of some interest.   By combining methyl-β-bromoethylaniline with ethylaniline, NN'-diphenyl-N-methyl-N'-ethylethylenediamine, NMePh·CH$_2$·CH$_2$·NEtPh, results, and the dinitroso-derivative of this when hydrolysed by means of

[61] G. T. Morgan and D. A. Cleage, *T.*, 1918, **113**, 588.
[62] G. T. Morgan and W. R. Grist, *ibid.*, 688.
[63] J. von Braun, K. Heider, and E. Müller. *Ber.*, 1917, **50**, 1637 ; 1918, **51**, 273, 737 ; *A.*, i, 107, 269, 406.

concentrated aqueous sodium hydrogen sulphite gives s-methyl-ethylethylenediamine, NHMe·CH$_2$·CH$_2$·NHEt, in good yield. The method appears to be of general application for the preparation of alkylated ethylenediamines of the type NHR·CH$_2$·CH$_2$·NHR'.

Anils.—K. von Auwers [64] discusses several cases where the condensation of aromatic aldehydes with substituted phenylhydrazines, semicarbazide, and aromatic amines gives an isolable additive compound as a first product in place of the anhydro-compound normally obtained, for example, R·CH(OH)·NH·R' instead of R·CH:N·R'. Whilst it is very rarely possible to pass back from the anhydro-compound to the hydrate, the closely related compounds of the type R·CH(OH)·NAcR can be prepared from many anils of substituted salicylaldehydes.

N-Acetyl-o-hydroxylaminobenzaldehyde.—Although o-hydroxyl-aminobenzaldehyde has not yet been isolated, owing to the readiness with which it decomposes into its anhydride, anthranil,

$$C_6H_4{<}^{NH·OH}_{CHO} \longrightarrow C_6H_4{<}^{N\text{---}}_{CH}{>}O,$$
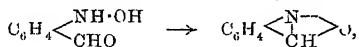
a method of preparation of its *N*-acetyl derivative has now been discovered.[65] When "agnotobenzaldehyde," the primary reduction product of o-nitrobenzaldehyde, is treated with acetic anhydride, it yields o-nitrobenzaldehyde and *N*-acetyl-o-hydroxylaminobenz-aldehyde in good yield. On heating to 125°, this compound suffers rearrangement, with the formation of acetylanthranilic acid,

$$CHO·C_6H_4·NAc·OH \longrightarrow CO_2H·C_6H_4·NHAc,$$
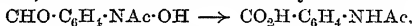
whilst on oxidation with a solution of bleaching powder it gives o-nitrosobenzaldehyde in good yield.

Aromatic Compounds of Tin, Lead, and Silicon.

The main products of the bromination of tin tetra-aryls alone or in organic media, even under the most careful conditions, are the tin diaryl dibromides. By employing pyridine as the solvent, however, the reaction can be stopped at the first stage, giving the tin triaryl bromide in a yield of 90—95 per cent. of the theoretical.[66]

Like the tin trialkyl bromides,[67] the tin triaryl bromides yield an ethereal solution of the corresponding hydroxide when shaken with ether and sodium hydroxide.

[64] *Ber.*, 1917, **50**, 1585 ; *A.*, i, 193.
[65] E. Bamberger, *ibid.*, 1918, **51**, 613 ; *A.*, i, 346.
[66] E. Krause, *ibid.*, 912 ; *A.*, i, 415.
[67] G. Grüttner and E. Krause, *ibid.*, 1917, **50**, 1802 ; *A.*, i, 158.

The use of pyridine is equally advantageous in the conversion of lead tetra-aryls into lead triaryl bromides by means of bromine, nearly theoretical yields being obtained, whereas previously under the most careful conditions the yield did not exceed 10 per cent. of the theoretical.[68]

By the action of magnesium aryl haloids on lead trialkyl haloids. lead aryl trialkyls have been prepared.[69]

$$Alk_3PbCl + ArMgCl \longrightarrow Alk_3PbAr$$
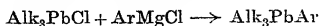
The magnesium p-halogenophenyl bromides derived from p-chlorobromobenzene and p-dibromobenzene react with silicon tetrachloride, yielding trichloro-p-halogenophenylmonosilanes, which give p-halogenophenyltrialkylmonosilanes when treated with magnesium alkyl haloids.[70]

$$C_6H_4Br \cdot SiCl_3 \qquad C_6H_4Br \cdot Si(Alk)_3.$$

These, again, react with magnesium, and the products can be employed in Grignard syntheses to give compounds containing silicon and also lead or tin. The magnesium compound of p-bromophenyltriethylmonosilane reacts with lead trimethyl bromide, giving p-triethylsilyltrimethylplumbylbenzene, $SiEt_3 \cdot C_6H_4 \cdot PbMe_3$, and with tin triethyl bromide, giving p-triethylsilyltriethylstannylbenzene, $SiEt_3 \cdot C_6H_4 \cdot SnEt_3$. The p-halogenophenyltrialkylmonosilanes can also be employed in syntheses by Fittig's method; thus, p-chlorophenyltriethylmonosilane reacts with chlorodiphenylarsine in the presence of sodium, forming p-diphenylarsyltriethylsilylbenzene, $SiEt_3 \cdot C_6H_4 \cdot AsPh_2$.

FRANK LEE PYMAN.

PART III.—HETEROCYCLIC DIVISION

OWING to the continuance of the war, a certain amount of overlapping has again been rendered necessary in the compilation of this Report. Certain papers published in foreign countries could not be dealt with last year, owing to the journals containing them not having reached this country in time to secure insertion of accounts of the work before the Report went to press. Where these papers seemed suitable for description, accounts of them have

[68] G. Grüttner, *Ber.*, 1918, **51**, 1298 ; *A.*, 1919, i, 52.
[69] Gerhard and Gertrud Grüttner, *ibid.*, 1293 ; *A.*, 1919, i, 52.
[70] G. Grüttner and E. Krause, *Ber.*, 1917, **50**, 1559 ; *A.*, i, 132.

been inserted in the present Report, although technically they belong to last year's work.

The general trend of the year's work appears to have been towards the study of natural products, mainly in the alkaloid group, and it is a hopeful sign that organic chemistry is once more turning back to its original field and is showing a weakening in the interest in purely synthetic research which at one time threatened to divorce it entirely from the naturally occurring materials.

In this branch of chemistry there is little room for much theoretical speculation, apart from constitutional problems, but attention may be directed to the suggestions which have been put forward with regard to the mechanism of the benzidine change.

The investigations centring about the connexion between chemical constitution and physiological action in the cocaine series are also of interest, as this problem is one of the most obscure that is touched on by organic chemistry.

For the rest, the paragraph headings will suffice to give an idea of the contents of the Report.

A Theory of certain Intramolecular Changes.[1]

Robinson and Mrs. Robinson[2] have put forward an hypothesis with regard to the mechanism of a peculiar intramolecular reaction which has been studied by them, and since their views also cover the mysterious case of the benzidine and semidine changes, they deserve a fairly full description here.

The authors assume as a basis the possibility of a partial dissociation of molecules, and when a molecule has undergone partial dissociation they term it "activated." Let A—b—c—D represent the structure of a molecule such that b or c (or both) are atoms capable of displaying a higher valency during salt-formation. The salt is now supposed to pass into the activated condition by the absorption of energy, and in these circumstances it may be represented by the following scheme, in which the acid is omitted for the sake of simplicity: A—$\overset{\vdots}{b}...\overset{\vdots}{c}$—$D$. Now, if the new partial valencies shown in this scheme are conjugated with unsaturated

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[1] In this connexion it seems desirable to point out the advantages of subtitles in the case of certain papers. This communication bears the title "A New Synthesis of Tetraphenylpyrrole," and thus no clue is given to the fact that it contains important theoretical considerations.

[2] Mrs. G. M. Robinson and R. Robinson, *T.*, 1918, **113**, 639.

groups in A or D, the molecule may be represented [3] by something like (I.) or (II.):

$$\text{(I.)} \quad A\!-\!b \cdots c\!-\!D \qquad\qquad A\!-\!b \cdots c\!-\!D \quad \text{(II.)}$$

Assume, now, a further conjugation of partial valencies in each case. The result will be, in case I, that A and c will become united, and if this be followed by the conversion of partial into complete dissociation at the junction of b and c, the result will be the formation of the new molecule $b\!-\!A\!-\!c\!-\!D$. In case II, the result will be a union between A and D accompanied by a separation of b and c, resulting as a whole in the formation of the new molecule $b\!-\!A\!-\!D\!-\!c$. It will be seen that the first case corresponds with the semidine change, whilst the second (double) shift corresponds with the benzidine rearrangement.

In practice, indole derivatives may be obtained from substituted hydrazines in a series of steps, which are shown in a simplified form below:
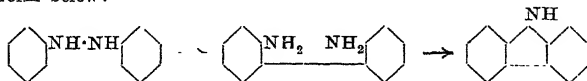
The mechanism of this is represented on the Robinson hypothesis as follows:
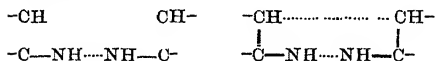
Partial dissociation.

Conjugation and ring-formation.

Further dissociation and conjugation.

Enamic form.

Enimic form.
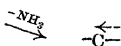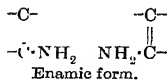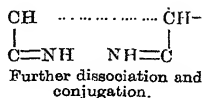
Indole derivative.
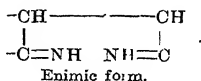
Further confirmation of the hypothesis is found in the fact that a new synthesis of tetraphenylpyrrole has been based on it. When

[3] The thickened lines stand for a normal valency plus a partial valency.

the azine of deoxybenzoin is treated with dry hydrogen chloride at 180°, it is converted almost quantitatively into a tetraphenyl-pyrrole and ammonium chloride:

$$Ph \cdot C{:}N \cdot N{:}CPh \qquad PhC \cdot NH \cdot NH \cdot CPh$$
$$Ph \cdot CH_2 \quad CH_2Ph \qquad PhCH \quad HCPh$$

$$PhC \cdot NH_2 \quad NH_2 \cdot CPh \qquad\qquad \overset{\displaystyle NH}{PhC \quad CPh}$$
$$PhC\text{———} \quad \text{———}CPh \qquad\qquad PhC\text{——}CPh$$
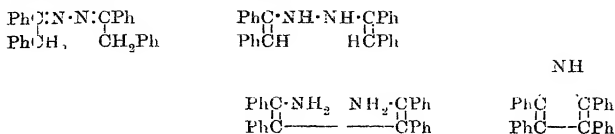
The Coumarin Group.

Some investigations [4] have been made with the object of determining the conditions which govern the opening of the coumaranone ring and the converse process of ring-formation from open-chain derivatives.

In the case of 1 : 4-dimethylcoumaranone, two possible types of opening reactions are known:
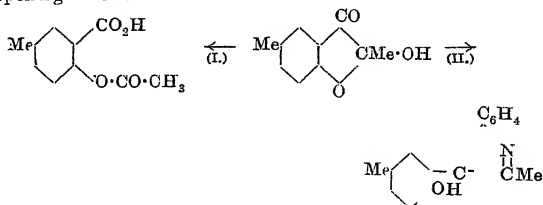
The reaction marked (I.) takes place when the coumaranone is allowed to oxidise spontaneously in air, whilst opening of the type (II.) occurs under the influence of reagents such as hydroxylamine, which react with a carbonyl group.

The first reaction is not suitable for the purpose of the investigation, since it appears to fail in the cases of more highly substituted coumaranones; but the second type has been utilised in order to study the effect of substitution, and it has been shown that substituents in the ortho- or para-position with respect to the oxygen atom have a weakening influence on the ring-stability, whilst meta-substituents have a strengthening effect. Turning to the problem of ring-formation, it is found that substitution exerts marked influence. When an o-α-halogenacylphenol of the type shown below is treated with alkali hydroxide, the reaction shown

[4] K. von Auwers and W. Müller, Ber., 1917, 50, 1149 ; A., i, 27.

in the formulæ takes place to a greater or less extent according to the nature of the radicle R.
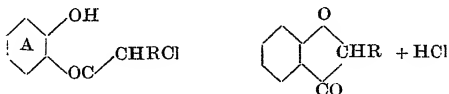
When the group A is a *m*-cresol nucleus and R is a propionyl radicle, the corresponding coumaranone is the main product of the reaction, although some α-hydroxypropionylcresol is also formed. When A is derived from *p*-cresol and R is a butyryl radicle, the condensation also yields the coumaranone ring; 6-chloroacetyl-5-*m*-xylenol condenses with the greatest of ease to form 3 : 5-dimethyl-coumaranone. On the other hand, *m*-α-bromo*iso*butyryl-*p*-cresol yields no coumaranone at all, being converted into either 3 : 6-di-methyl-1 : 4-benzopyrone or *m*-α-hydroxy*iso*butyryl-*p*-cresol.

It has now been shown[5] that when benzoacetodinitrile is con-densed with resorcinol under the influence of hydrogen chloride, the product is not 3-hydroxyflavone, but 7-hydroxy-4-phenyl-coumarin.

A very simple method[6] has been devised for the production of hydroxycoumaranones, which may be illustrated by the specific case of the dihydroxy-derivative. Phloroglucinol and chloroaceto-nitrile are dissolved in ether, and the solution is saturated with hydrogen chloride, by which means the hydrochloride of a keto-imide is precipitated. On boiling this product with water, it is hydrolysed, and forms the required coumaranone :
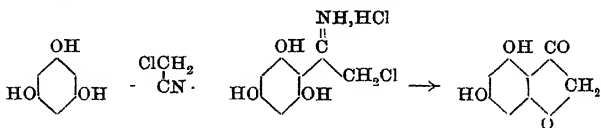
A new type of coumarin derivative has been obtained[7] in which a *cyclo*propane ring forms part of the nucleus. For example, when 3-acetylcoumarin and ω-halogenacetophenones are treated with sodium ethoxide in cold alcoholic solution, two products result, which have the structures
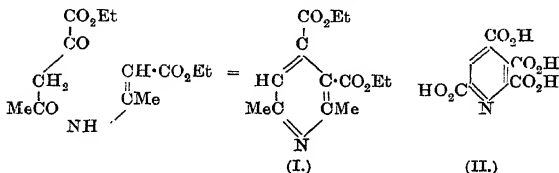
[5] A. Sonn, *Ber.*, 1918, **51**, 821 ; *A.*, i, 401.
[6] *Idem*, 1917, **50**, 1262, 1292 ; *A.*, i, 31.
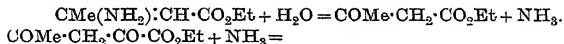[7] O. Widman, *ibid.*, 1918, **51**, 533 ; *A.*, i, 347.

The compounds are not acted on by permanganate, as is the original coumarin, owing to the fact that the ethylenic linking disappears from the coumarin ring in the course of their formation. The reaction appears to be a general one.

The Pyridine Group.

A new general reaction for the synthesis of various pyridine polycarboxylic acids has been worked out.[8] In its essentials, it consists in the condensation of acetylpyruvic ester or its homologues with compounds such as β-aminocrotonic ester. In the case of ethyl acetylpyruvate and β-aminocrotonic ester, if the reaction is carried out at 0° a pyridine derivative is formed:

$$
\begin{array}{ccc}
\underset{\substack{|\\ \text{CO}\\ |\\ \text{CH}_2\\ |\\ \text{MeCO}}}{\text{CO}_2\text{Et}} \quad \underset{\substack{\text{CH·CO}_2\text{Et}\\ ||\\ \text{CMe}}}{} \quad \underset{\text{NH}}{} & = & \underset{\substack{\text{C}\\ |\\ \text{HC} \quad \text{C·CO}_2\text{Et}\\ || \quad ||\\ \text{MeC} \quad \text{CMe}\\ \diagdown N \diagup}}{\text{CO}_2\text{Et}} \qquad \underset{\substack{\text{CO}_2\text{H}\\ \\ \text{CO}_2\text{H}\\ \text{HO}_2\text{C} \quad \text{CO}_2\text{H}\\ N}}{}
\end{array}
$$

$$\text{(I.)} \qquad\qquad \text{(II.)}$$

When the mixture is allowed to become warm, however, other reactions occur which reduce the almost quantitative yield considerably.

$$\text{CMe(NH}_2)\text{:CH·CO}_2\text{Et} + \text{H}_2\text{O} = \text{COMe·CH}_2\text{·CO}_2\text{Et} + \text{NH}_3.$$

$$\text{COMe·CH}_2\text{·CO·CO}_2\text{Et} + \text{NH}_3 =$$

$$\text{COMe·CH}_2\text{·C(:NH)·CO}_2\text{Et} + \text{H}_2\text{O}.$$

From the dimethylpyridinedicarboxylic acid (I) it is possible, by oxidation with permanganate, to produce a tetracarboxylic acid (II), so that the method lends itself to the production of a varied series of compounds. Not only so, but by distilling the acid (I) with calcium hydroxide, a 91 per cent. yield of 2 : 6-lutidine can be obtained. This method appears to be the most convenient way of preparing pure lutidine that has yet been devised.

Some derivatives of the pyridine series have been described which are formed by the action of $\alpha\beta$-dichloroethyl ether on aminocompounds.[9] Thus, in the case of the reaction between $\alpha\beta$-dichloroethyl ether and ethyl β-aminocrotonate, the product is ethyl 2 : 6-dimethyl-4-chloromethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate.

[8] O. Mumm and H. Hüneke, Ber., 1917, 50, 1568 ; 1918, 51, 150 ; A., i, 183, 184.

[9] E. Benary, ibid., 1918, 51, 567   A., i, 350.

The Relative Stability of Cyclic Bases.

In last year's Report [10] it was pointed out that cyclic bases may be converted into open-chain compounds either by exhaustive methylation or by the action of cyanogen bromide, and that the two reactions appeared to give similar results when used as tests of the stability of the rings in cyclic bases. It now appears [11] that dihydroindole forms an exception to the general rule, as it is very stable in the Hofmann reaction, but is readily attacked by cyanogen bromide. With the latter reagent, the reaction takes the following form:

$$C_6H_4{<}^{CH_2-}_{NMe}{>}CH_2 + BrCN \longrightarrow \left\langle \begin{array}{c} CH_2 \cdot CH_2Br \\ NMe \cdot CN \end{array} \right. +$$

$$C_6H_4{<}^{CH_2-}_{N(CN)}{>}CH_2 + MeBr .$$
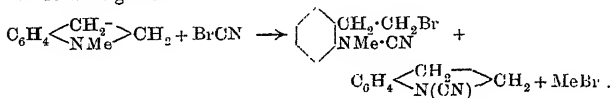
The morpholine ring [12] appears to rank along with tetrahydroisoquinoline and dihydroisoquinoline when tested with cyanogen bromide, whilst by the test of the Hofmann reaction it stands midway between the two.

The theory of ring-closure has also been further investigated,[13] but the results appear to be of little general interest.

A New Synthesis of Acridine.

When 1-aminoanthraquinone and o-chlorobenzaldehyde are allowed to condense together in the presence of copper powder and dry sodium carbonate at 220°, the reaction does not follow the

Not formed.

Formed in reaction.
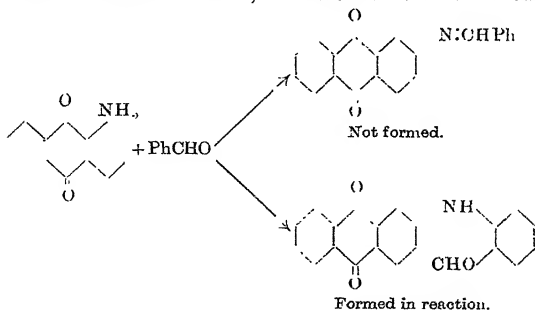
[10] Ann. Report, 1917, 130.
[11] J. von Braun, Ber., 1918, 51, 96 ; A., i, 185.
[12] J. von Braun and Z. Köhler, ibid., 255 ; A., i, 268.
[13] R. Meyer and H. Lüders, Annalen, 1918, 415, 29 ; A., i, 450.

usual course with the production of a Schiff's base, but, instead, o-1-anthraquinonylaminobenzaldehyde appears among the products.

The abnormal course of this reaction is attributed [14] to a mutual influence between the carbonyl radicle and the adjacent amino-group, which leads to a repression of the basic function of the latter. In order to test this view, other compounds were examined, in which the amino-group is similarly situated with regard to "negative" groups, and it has been shown that a nitro-group in the ortho-position leads to an abnormal reaction, whilst nitro-groups in the meta- and para-positions seem to have no such effect. (The last result appears curious in view of the recognised influence of certain para-substituents on one another.)

From the o-nitroanilinobenzaldehydes produced by this reaction, nitroacridines can be obtained by means of concentrated sulphuric acid. In order to obtain acridine itself, iodobenzene and o-aminobenzaldehyde are boiled together in nitrobenzene with sodium carbonate and copper powder. The solvent is removed with steam, and sulphuric acid is added:
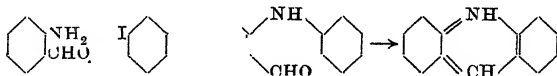
isoBrazilein.

When brazilin, $C_{16}H_{14}O_5$, is oxidised, it yields the quinone, brazilein, $C_{16}H_{12}O_5$, and by the action of mineral acids, the quinone is converted into a series of orange-red salts, which are termed isobrazilein salts. The constitutions provisionally assigned to these substances are shown below:
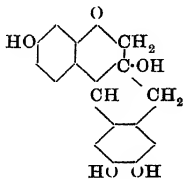
Brazilin.
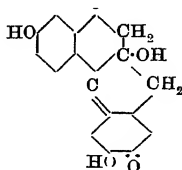
Brazilein.

[1] F. Mayer and B. Stein, Ber., 1917, 50, 1306 ; A., i, 36.

SO_4H

HO ... CH

C CH_2

HO OH
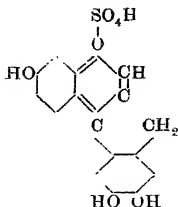
Brazilein hydrogen sulphate.

Some of these *iso*brazilein salts have now been synthesised in the following manner.[15] Paeanol and veratraldehyde were condensed together, and the product was reduced catalytically to the dihydro-derivative, dihydrobutein trimethyl ether. By prolonged boiling with zinc chloride and a large excess of absolute formic acid, the trimethyl ether gave rise to a product from which *iso*brazilein ferrichloride trimethyl ether could be isolated. Demethylation

OH

MeO ... $H \cdot CO_2H$

CH_2

CO CH_2

MeO OMe

O

MeO ... $CH \cdot OH$

C CH_2

MeO OMe
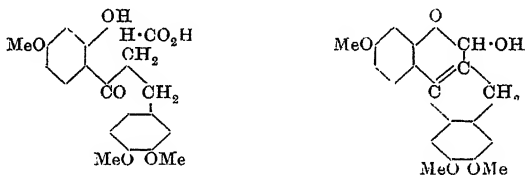
was then carried out by heating the trimethyl ether salt with hydrochloric acid at 150° in a sealed tube, and the end-product showed all the reactions of *iso*brazilein hydrochloride.

The Isatin Group.

When the *N*-sodium derivative of isatin is treated with methyl or ethyl chloroformate, the corresponding isatin-1-carboxylic ester is produced.[16] If these esters are boiled with water or treated with acids under certain conditions, they yield an acid which contains four hydrogen atoms more than the parent 1-carboxylic acid. This new substance does not give the indophenin reaction, and on exposure to air in alkaline solution it yields isatinic acid with ease. (During the reaction of decomposition, the methyl ester liberates

[15] H. G. Crabtree and R. Robinson, *T.*, 1918, **113**, 859.
[16] G. Heller. *Ber.*, 1918, **51**, 424 ; *A.*, i. 309.

formaldehyde, and the ethyl ester produces acetaldehyde.) Apparently the acid thus formed has the structure
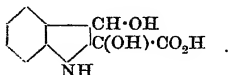

In ordinary circumstances, it is not easy to reduce an indole to the corresponding dihydro-compound, so that the effect of introducing a carbalkyloxy-group into the molecule is followed by a marked increase in reactivity on the part of the compound.

The author draws a parallel between the ease with which this reduction takes place and the readiness with which enzyme action occurs, but it seems to be a somewhat fanciful view of the case.

The new acid exhibits another curious reaction when it is oxidised with potassium dichromate and dilute sulphuric acid, for the product is said to be a quinolinecarboxylic acid having the structure

$$C_6H_4 \diagdown \begin{matrix} CH(OH) \cdot CH_2 \\ NH \text{———} C(OH) \cdot CO_2H \end{matrix}$$
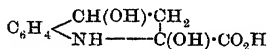
It will be noted that this result corresponds with the accretion of an extra methylene group and the transformation of a five- into a six-membered ring. If the extra carbon atom can be successfully accounted for, there seems to be little difficulty about the remainder of the change, since cases of the kind are already known, the most similar being that noted by Meiser,[17] wherein the pinacone (I) is converted into the pinacolin (II) on treatment with dilute
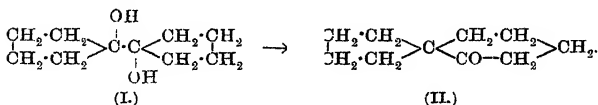
sulphuric acid. It seems scarcely necessary to resort to hypothesis of "pseudo-enzymatic action" to account for the results.

The Purine Group.

A very full study of the oxidation of uric acid by means of hydrogen peroxide [18, 19] has produced interesting results. It appears

[17] W. Meiser, Ber., 1890, 32, 2054 ; A., 1899, i, 741.

[18, 19] C. S. Venable and F. J. Moore, J. Amer. Chem. Soc., 1917, 39, 1750 ; C. S. Venable, ibid., 1918, 40, 1099 ; F. J. Moore and R. M. Thomas, ibid., 1120 ; A., i, 104, 409, 410.

that under the conditions which were supposed to lead to the formation of tetracarbimide, this compound is not obtained, for the main product is found to be cyanuric acid. It seems likely, therefore, that the so-called tetracarbimide was really cyanuric acid.

The reaction between hydrogen peroxide and uric acid is a complex one. In weakly alkaline solutions at temperatures near 100°, allantoin appears to be the first product, for it is produced in large quantities at the beginning of the reaction and is accompanied only by minor proportions of carbonyldicarbamide. These two compounds seem to be the result of two different reactions, since they appear to be produced in arbitrary proportions. The further progress of the reaction is marked by the amount of the carbonyldicarbamide remaining fairly constant, whilst the yield of allantoin rapidly decreases. Meanwhile, increasing amounts of cyanuric acid make their appearance up to about 10 per cent. It is found that increasing alkalinity of the solution favours the formation of cyanuric acid—even as much as 50 per cent. being formed under good conditions—whilst the yields of allantoin and carbonyldicarbamide are proportionately diminished.

It might be supposed that the cyanuric acid is formed from the allantoin, which is the primary product of the reaction, but this appears to be negatived by the fact that under the same conditions of experiment no cyanuric acid is formed directly from allantoin; also, since the highest yield of carbonyldicarbamide observed can only, assuming its complete conversion into cyanuric acid, bring the percentage of the latter up to thirty, it will be seen that two-fifths of the cyanuric acid remains unaccounted for.

It is evident that the reaction between hydrogen peroxide and uric acid takes a different course, according to the temperature and the alkalinity of the solution in which it is carried out.

Apparently an intermediate product occurs, as is shown by the following evidence. The alkaline solution resulting from the oxidation was treated with manganese dioxide, whereby the excess of hydrogen peroxide was destroyed. After neutralisation, a 60 per cent. yield was obtained of the salts of a dibasic acid, $C_4H_5O_5N_3$, which may possibly be hydrated allantoxanic acid, $C_4H_3O_4N_3,H_2O$. This acid, when oxidised in acid solution by means of hydrogen peroxide, gives an 80 per cent. yield of cyanuric acid.
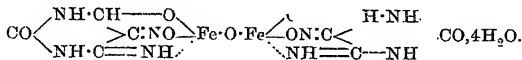
Chromoisomerism.

It will be recalled that when the salts of a base and an acid occur in varieties exhibiting different colours the phenomenon has

been described by Hantzsch as chromoisomerism. The field has proved a captivating one to those who delight to speculate on "possible" or "theoretical" structures for given molecules, but it seems time to protest against one halfpennyworth of practice to this intolerable deal of theory, and to demand something more than assertion in proof of the constitutional formulæ which are drawn up so lavishly.

The latest example of this spirit is to be found in a paper on iminovioluric acid.[20] The free acid has been isolated in three forms. With mineral acids, iminovioluric acid forms colourless salts; with alkalis or alkaline earths, pink or red salts are produced. So much for practice. On these scanty data and on the strength of absorption spectra curves the authors proceed to raise a mass of speculation, which becomes at times detached from reality. Four formulæ are given as "theoretically possible" for iminovioluric acid, but at least two other structures are equally "theoretically possible," and it seems curious not to find them considered also when stereoisomerides are included in the four actually dealt with. Since the metallic salts of iminovioluric acid have absorption spectra similar to those of the violurates, it is laid down that the nitroso-group is modified and involved in the establishment of a "residual affinity ring." There seems to be no evidence for this, unless something definite can be adduced as to the constitution of the violurates. All that the spectra prove is that probably the exchange of the group ·CO· for the group ·C(:NH)· produces no great alteration in the spectra.

Again, if the sodium salt is reduced with ferrous sulphate, a dark blue powder can be obtained as a precipitate. It is stated that it may be represented by

$$CO \begin{cases} NH\cdot CH \text{-----} O \\ NH\cdot C \text{===} NH \end{cases} C:NO \text{-} Fe\cdot O\cdot Fe \begin{cases} ON:C \\ NH \text{===} C \text{---} NH \end{cases} H\cdot NH \\ CO,4H_2O.$$

It may be, but the evidence scarcely seems convincing.

The Areca Nut Alkaloids.

Our knowledge of the alkaloids yielded by the areca or betel nut has advanced considerably, and the constitution of these compounds seems to be almost established by the work of the past year.[21] Apparently the nut is rich in related alkaloids, for the

[20] I. Lifschitz and L. Kritzmann, *Ber.*, 1917, **50**, 1719 ; *A.*, i, 192.
[21] K. Hess and F. Leibbrandt, *ibid.*, 1918, **51**, 806 ; *A.*, i, 401 ; K. *ibid.*, 1004 ; *A.*, i, 403 ; K. Freudenberg, *ibid.*, 978 ; *A.*, i, 403.

following have been detected in it: arecaidine, arecoline (arecaidine methyl ester), guvacine, arecaine (*N*-methylguvacine), and guvacoline (guvacine methyl ester).

Arecaine has been definitely proved to be the guvacine *N*-methyl derivative, since it is formed by the action of formaldehyde and formic acid on guvacine. Arecoline has already been prepared by esterifying arecaidine with methyl alcohol. Guvacoline has been converted into guvacine and vice versa by esterification or hydrolysis.

Doubt still remains as to the exact constitution of these alkaloids, however, for although arecaidine was synthesised some time ago, the method employed does not settle the structure of the end-product. Hess regards guvacine as 1:2:5:6-tetrahydropyridine-4-carboxylic acid, whilst Freudenberg believes that the carboxyl radicle occupies the 3-position. The evidence appears to incline toward the former view, since the reduction of guvacine yields piperidine-4-carboxylic acid.

Two curious reactions may be mentioned in this connexion. When arecaine (*N*-methylguvacine) is boiled with alcoholic hydrogen chloride, it loses its methyl group and yields the ethyl ester of guvacine. Again, guvacoline (guvacine methyl ester) is said to yield arecaidine when its methiodide is hydrolysed. This implies that arecaine and arecaidine are identical,· although possibly they may be stereoisomerides. Further work on the point will be of interest.

Some negative evidence on the problem is obtained from the results obtained in the course of the reduction of nicotinic acid derivatives.[22] When trigonelline (I) is reduced with hydrogen in the presence of platinum black and the product subjected to the action of methyl iodide, the result is the formation of an *N*-methyl derivative (II) which gives a platinichloride having the same melting point as the platinichloride of arecaidine. The aurichloride

(I.)   (II.)
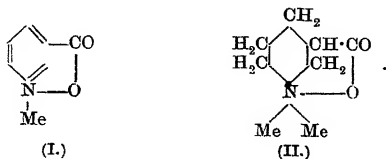
and the picrate of the new base, however, are not identical with the corresponding arecaidine derivatives. It seems certain, there-

[22] E. Winterstein and A. B. Weinhagen, *Zeitsch. physiol. Chem.*, 1917, **100**, 170; *A.*, i, 35.

fore, from this and other evidence that arecaidine cannot have the formula (II), although it may have a very similar structure.

Alkaloids of the Pomegranate Tree.

The clearing up of this field really belonged to last year's Report, but owing to war conditions it was impossible to take note of it in that place, and it is therefore dealt with here. It has now been proved [28] that pelletierine is β-2-piperidylpropaldehyde, or, in other words, the aldehyde of coniine:

$$CH_2$$

$$CH_2 \quad CH_2$$
$$CH_2 \quad CH \cdot CH_2 \cdot CH_2 \cdot CHO$$
$$NH$$
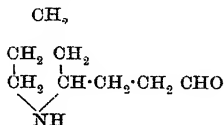
Curiously enough, although pelletierine is a secondary base, it does not react with nitrous acid. This behaviour has been attributed to the mutual influences of the nitrogen atom and the aldehyde group, which, as can be seen from the formula, stand in the 1:5-position with regard to each other.

The pelletierine group is suffering from the changes of nomenclature which seem inseparable from alkaloidal research. Tanret isolated an inactive base which he termed *iso*pelletierine, but this has now been rechristened pelletierine by Hess and Eichel. Tanret's methylpelletierine has similarly been renamed methyl*iso*-pelletierine.

This methyl*iso*pelletierine has the formula $C_9H_{17}ON$, and has been shown to be a tertiary base containing a carbonyl radicle. When its hydrazone is heated with sodium ethoxide solution in a sealed tube, 1-methylconiine is produced. This reaction limits the choice of a formula for methyl*iso*pelletierine, since it must have the constitution $CH_2{<}^{CH_2-CH_2}_{CH_2 \cdot NMe}{>}CHR$, in which R is either $\cdot CH_2 \cdot CH_2 \cdot CHO$ or $\cdot CH_2 \cdot COMe$ or $\cdot COEt$.

The first two alternatives are ruled out, since they correspond respectively with methylpelletierine and α-1-methylpiperidyl-2-propan-β-one, both of which are already known. Methyl*iso*-pelletierine is therefore an ethyl ketone. A further change in nomenclature seems justified in this case.

The solution of the methyl*iso*pelletierine problem has brought with it the determination of the conhydrine structure, for con-

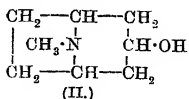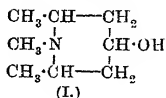[28] K. Hess and A. Eichel, *Ber.*, 1917, **50**, 1192, 1386 ; *A.*, i, 33, 34.

hydrine can be converted into methyl*iso*pelletierine, and must, in order to make the reaction possible, be assumed to be α-2-piperidyl-propyl alcohol.

One point of interest in the stereochemical field is raised by the pelletierine derivatives. Originally it was believed that the alkaloids of the pomegranate root were optically active, but it seems to be now proved that they are entirely racemic, no active substances being found. In the great majority of cases, vital syntheses lead to the preponderance of one or other antipode in the product, but apparently the natural synthesis of pelletierine is a symmetrical process, or else the plant must possess the power of racemising the active alkaloid after its formation. The racemisation of the free bases is apparently not likely to be spontaneous, since they can be distilled without marked change in their rotatory power.[24]

Cocaine and its Allies.

One of the most puzzling problems which confronts the investigator is that which is concerned with the physiological action of certain compounds. At the present time, the experimental evidence is confusing and incomplete to such an extent that it is almost impossible to draw any conclusions of value from it, and it is therefore of great interest to find that a systematic study of even a restricted class of compounds has been made.[25]

It appears probable that the physiological activity of cocaine itself is in some way connected with the presence of the acylated hydroxyl group in the γ-position with regard to the nitrogen atom in the ring, for the *N*-methylvinyldiacetonealkamines of the structure (I) have a pharmacological action very similar to that of tropine, (II). wherein a similar grouping occurs :

$$
\begin{array}{ll}
CH_3 \cdot CH \!\!-\!\! CH_2 & CH_2 \!\!-\!\! CH \!\!-\!\! CH_2 \\
CH_3 \cdot N \quad\; CH \cdot OH & \quad CH_3 \cdot N \quad\; CH \cdot OH \\
CH_3 \cdot CH \!\!-\!\! CH_2 & CH_2 \!\!-\!\! CH \!\!-\!\! CH_2 \\
\quad\quad (I.) & \quad\quad (II.)
\end{array}
$$

It therefore remains to be seen whether this characteristic is affected when the acylated hydroxyl radicle in cocaine is transferred to another point in the molecule while still retaining the γ-position with regard to the nitrogen atom.

This has now been done in the following manner. Cocaine

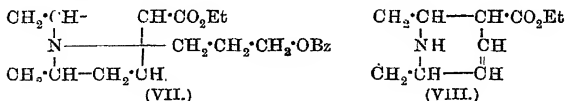[24] K. Hess and A. Eichel, *Ber.*, 1918, 51, 741 ; *A.*, i, 404.
[25] J. von Braun and E. Müller, *ibid.*. 235 ; *A.*, i, 233.

(III) is converted by known methods into ecgonidine (anhydro-ecgonine), the ethyl ester of which has the structure (IV). By reducing this first with hydrogen and palladium, and subsequently with sodium and amyl alcohol, a new base, homotropine (V), is formed, which is then converted into the tropic acid derivative (VI). It is found that the mydriatic action of this substance is quite as powerful as that of cocaine itself.

$$
\begin{array}{cc}
\text{CH}_2\cdot\text{CH}\!-\!\!-\!\!\text{CH}\cdot\text{CO}_3\text{Me} & \text{CH}\cdot\text{CH}\!-\!\!-\!\!\text{CH}\cdot\text{CO}_2\text{Et} \\
\quad | \qquad | & \qquad | \qquad | \\
\text{NMe} \quad \text{CH}\cdot\text{OBz} & \text{NMe} \quad \text{CH} \\
\quad | \qquad | \qquad \longrightarrow & \qquad | \qquad | \\
\text{CH}_2\cdot\text{CH}\!-\!\!-\!\!\text{CH}_2 & \text{H}_2\cdot\text{CH}\!-\!\!-\!\!\text{CH} \\
\text{(III.)} & \text{(IV.)}
\end{array}
$$

$$
\begin{array}{cc}
\text{CH}_2\cdot\text{CH}\!-\!\!-\!\!\text{CH}\cdot\text{CH}_2\cdot\text{OH} & \text{CH}_2\cdot\text{CH-} \quad \text{-CH}\cdot\text{CH}_2\cdot\text{O} \\
\quad | \qquad | & \qquad | \qquad | \qquad | \\
\text{NMe} \quad \text{CH}_2 & \text{NMe} \quad \text{CH}_2 \quad \text{CO} \\
\quad | \qquad | & \qquad | \qquad | \qquad | \\
\text{CH}_2\cdot\text{CH}\!-\!\!-\!\!\text{CH}_2 & \text{CH}_2\cdot\text{CH}\!-\!\!-\!\!\text{CH}_2 \quad \text{C}_8\text{H}_9\text{O} \\
\text{(V.)} & \text{(VI.)}
\end{array}
$$
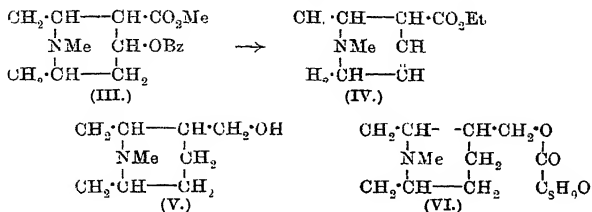
This clearly indicates that the mydriatic effect of cocaine is not affected by the transfer of the acylated hydroxyl radicle from one carbon atom to a fresh one, provided that its γ-position with regard to the nitrogen atom is retained.

A different variation of the groups is shown in the compound VII, wherein also the acylated hydroxyl radicle is situated in the γ-position with respect to the nitrogen atom, although in this case the hydroxyl group is completely detached from the ring:

$$
\begin{array}{cc}
\text{CH}_2\cdot\text{CH-} \quad \text{CH}\cdot\text{CO}_2\text{Et} & \text{CH}_2\cdot\text{CH}\!-\!\!-\!\!\text{CH}\cdot\text{CO}_2\text{Et} \\
\quad | \qquad\qquad | & \qquad | \qquad | \\
\text{N}\!-\!\!-\!\!-\!\!-\!\! | \!-\! \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OBz} & \text{NH} \quad \text{CH} \\
\quad | \qquad\qquad | & \qquad | \qquad | \\
\text{CH}_2\cdot\text{CH}\!-\!\text{CH}_2\cdot\text{CH}. & \text{CH}_2\cdot\text{CH}\!-\!\!-\!\!\text{CH} \\
\text{(VII.)} & \text{(VIII.)}
\end{array}
$$

The last substance has been obtained by a complicated series of reactions which it is unnecessary to describe, and it is found that as a local anæsthetic it is quite as powerful as cocaine itself.

Evidently it must be concluded that the essential feature of the tropine group from the pharmacological point of view lies in the relative positions of the nitrogen atom and the hydroxyl radicle, for the case of the alkamines quoted above proves that the bridged ring structure of tropine is not indispensable to the activity.

In the course of this investigation, a useful compound has been isolated, which is termed eccaine and has the structure VIII. It is more active than cocaine in its anæsthetic properties, and has the additional advantages of being non-toxic and sufficiently stable to render its sterilisation easy.

An examination has also been made[26] of various compounds derived from alkaloids of the cocaine group by demethylation of the nitrogen atom, and it has been found that they have considerable activity, resembling cocaine in pharmacological action, and having the same advantages as eccaine in respect of stability and ease of sterilisation.

A very curious case[27] has been discovered in the reductions of tropinone (I) and ψ-pelletierine (II).

$$
\begin{array}{cc}
\text{CH}_2\cdot\text{CH- -CH}_2 & \text{CH}_2\text{---CH----CH}_2 \\
\dot{\text{N}}\text{Me } \dot{\text{C}}\text{O} & \dot{\text{C}}\text{H}_2 \quad \dot{\text{N}}\text{Me } \dot{\text{C}}\text{O} \\
\dot{\text{C}}\text{H}_2\cdot\dot{\text{C}}\text{H---CH}_2 & \dot{\text{C}}\text{H}_2\text{---CH---CH}_2 \\
\text{(I.)} & \text{(II.)}
\end{array}
$$
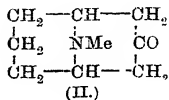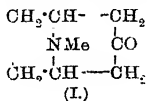
Reduction with hydriodic acid or electrolytically produces from tropinone the physiologically *active* tropine, whilst ψ-pelletierine yields by the same methods the physiologically *inert* *iso*methylgranatoline. When the reduction is carried out with sodium and alcohol, the results are reversed. Tropinone gives physiologically *inactive* ψ-tropine, whilst ψ-pelletierine yields the active product methylgranatoline.

When tropine is heated with concentrated hydriodic acid and excess of phosphonium iodide at 200°, it is reduced to tropane. The same end-product is obtained when hydroscopoline is similarly treated, and from this it is deduced[28] that scopoline and hydroscopoline are tropane derivatives, hydroscopoline being regarded as a dihydroxytropane.

Allies of Berberine.

A new system of nomenclature has been proposed for the compounds of the berberine group,[29] but as the formulæ take up a considerable amount of space, reference must be made to the original paper for details.

An account is given of various attempts to produce a compound which has been termed *epi*berberine. The new substance is isomeric with berberine, and differs from it inasmuch that the methylenedioxy- and dimethoxy-groups in berberine are transposed in *epi*berberine. A study of some derivatives of berberine closely allied to cryptopine[30] has been made, but the paper does not lend itself to summarisation.

[26] Chemische Werke Grenzach, *D.R.-P.*, 301139; *A.*, i, 121.

[27] L. F. Werner, *J. Amer. Chem. Soc.*, 1918, **40**, 669; *A.*, i, 267.

[28] K. Hess, *Ber.*, 1918, **51**, 1007; *A.*, i, 404.

[29] W. H. Perkin. jun., *T.*, 1918, **113**, 492.   [30] *Ibid.*, 722.

The Cinchona Alkaloids.

Progress towards the complete synthesis of quinine is being slowly made, and in the present year a gap in the series of reactions has been bridged by the conversion of quinicine (quinotoxine) into quinine.[31]

It will be recalled that when quinine and cinchonine are heated with dilute acetic acid, they are converted, respectively, into quinotoxine and cinchotoxine. The reaction is believed to consist in the conversion of a bridged ring into an unbridged one, as shown in the formulæ

The reverse change has now been accomplished in the following manner. Quinicine (quinotoxine), when treated with sodium hypobromite, furnishes N-bromoquinicine. Further treatment with alkali hydroxide yields the corresponding ketone, quininone, and when this is reduced with aluminium powder and sodium ethoxide solution, quinine is formed. The following formulæ indicate the nature of the process:

$$-CO\cdot CH_2- \quad -CO\cdot CH_2\cdot R \quad -CO\cdot CH\cdot R \quad -CH(OH)\cdot CH\cdot R$$
$$-NH- \quad -N Br- \quad \longrightarrow \quad -N- \quad -N-$$
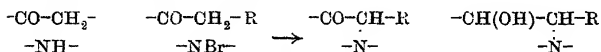
It is true that this step leaves many others still to be accomplished, but it is none the less satisfactory to see even a small advance made in this difficult problem.

With regard to the other half of the quinine molecule, which is derived from quinoline, some synthetic progress is being made in the direction of the production of the cinchonic acids,[32] but the results up to the present scarcely justify detailed description, as they are mainly tentative.

The complexity of the cinchona alkaloid problem becomes greater with increased research, owing to the number of possible isomerides which are obtained. Thus, when cinchonine is heated on a waterbath with hydrobromic acid there are formed, in addition to hydrobromocinchonidine, no fewer than five compounds, namely, cinchonigine, δ-cinchonine, apocinchonine, cinchoniline, and

[31] P. Rabe and K. Kindler, Ber., 1918, 51, 466; A., i, 303.
[32] A. Kaufmann, ibid., 116; A., i, 187.

cinchoniretine.[33] It is assumed that cinchonigine and cinchoniline
have the constitution represented by (I), whilst *apo*cinchonine is
regarded as possessing the structure (II), and on this basis it is
possible to explain the fact that these three compounds and
cinchonine itself will yield the same hydrobromocinchonine, as they
are found to do in practice.

$$\begin{matrix} \text{CHMe} \cdot [C_{16}H_{17}N \vdots CH] \\ | \hspace{2.5cm} | \\ O \underline{\hspace{2.3cm}} O \end{matrix}$$

$$CHMe \vdots C_{16}H_{16}N_2 \vdots CH \cdot OH \quad .$$

(I.)   (II.)
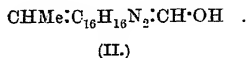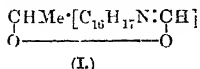
The action of hydrogen bromide, however, is not so simple as
might be anticipated, for, owing to the optical activity of the com-
pounds, it is necessary to assume that the additive reaction is
preceded by certain stereoisomeric changes. From the complexity
of the results of this simple reaction, it is possible to gauge the
difficulties of the cinchonine investigations.

A study of the behaviour of α-hydroxycinchonine has led Léger[34]
to the conclusion that the compound has the constitution repre-
sented by $CH_3 \cdot CH(OH) \cdot [C_{16}H_{17}N_2(CH \cdot OH)]$, but for the evidence
adduced by him, reference must be made to the original paper.

The Ipecacuanha Alkaloids.

This field appears to be now almost cleared up. In last year's
Report,[35] a table was given showing the relations existing between
the various substances of importance. It was already known that
the reduction of methylpsychotrine yielded both emetine and
*iso*emetine, and it is now found that oxidation of either emetine
or *iso*emetine leads to the formation of psychotrine and rubr-
emetine.[36] This apparently establishes the fact that emetine and
*iso*emetine are stereoisomerides, although the attempt to convert
one into the other has not been successful. It has further been
shown that *iso*emetine is the methyl ether of *iso*cephaeline. A
complete table of relations between the various derivatives is given
in the paper, but need not be reproduced here.

In physiological action, the two stereoisomerides emetine and
*iso*emetine differ from one another considerably, emetine being
much more toxic than *iso*emetine. Such differences are, of course,
fairly common.

[33] E. Léger, *Compt. rend.*, 1918, **166**, 76, 255, 469 ; *A.*, i, 121, 182, 232.
[34] *Ibid.*, **166**, 903 ; *A.*, i, 304.
[35] *Ann. Report*, 1917, 139.   [36] F. L. Pyman, *T.*, 1918, **113**, 222.

Carnosine and Histidine.

The constitution of carnosine is now placed beyond doubt. both by indirect methods and by direct synthesis.[37] The choice of a formula for the compound was limited to β-alanylhistidine (I) and histidyl-β-alanine (II).

$$\begin{matrix} NH \cdot CH \\ CH = N \end{matrix} > C \cdot CH_2 \cdot CH(NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot NH_2) \cdot CO_2H.$$

(I.)

$$\begin{matrix} NH \cdot CH \\ CH = N \end{matrix} > C \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot CO_2H.$$

(II.)
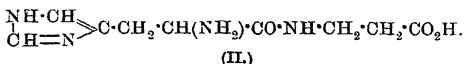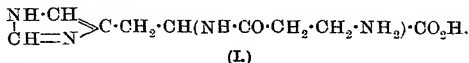
The indirect evidence was obtained by eliminating the amino-radicle and then hydrolysing the product, with the result that about 70 per cent. of the theoretical yield of histidine was obtained. Obviously, had the formula II been the correct one, no such effect could have been produced, since the histidine molecule contains the eliminated amino-group.

Carnosine was then synthesised in the following manner. β-Iodo-propionyl chloride was allowed to act on histidine, and the product was treated with ammonia, whereby the iodine atom is displaced by the amino-group.

A convenient method of preparing histidine from red blood corpuscles has been described.[38]

Ricinine.

A certain amount of evidence has been brought forward[39] to prove that ricinine is a glyoxaline derivative having the structure

$$\begin{matrix} CO_2Me \cdot C = C \cdot CH \\ | \quad N \quad | | \\ NMe \cdot C \cdot CH \end{matrix}$$
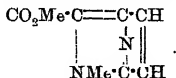
On hydrolysis with dilute potassium carbonate, ricinine yields the parent acid, ricininic acid, which can be reduced with sodium amalgam to a dihydro-derivative. This gives a coloration with ferric chloride characteristic of glyoxalinecarboxylic acids. No tetrahydro-derivative was obtained, which also favours the glyoxaline hypothesis. On oxidation with chromic and sulphuric

[37] L. Baumann and T. Ingvaldsen, *J. Biol. Chem.*, 1918, **35**, 263; *A.*, i, 454.
[38] H. M. Jones, *ibid.*, **33**, 429; *A.*, i, 232.
[39] B. Böttcher, *Ber.*, 1918, **51**, 673; *A.*, i, 304.

acids, ricininic acid yields methylamine, oxalic acid, and hydrogen cyanide, thus behaving like the other glyoxaline derivative, histidine. Fuming hydrochloric acid degrades ricininic acid to a pyridone derivative, the formula of which has been proved to be

$$N Me \underset{CH:C(OH)}{\overset{CH = CH}{<}} CO.$$
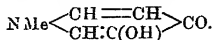
The evidence seems sufficient to show that ricinine belongs to the glyoxaline group.

Haemin.

Three papers on hæmin[40] were published last year too late for notice in the 1917 Report. In past years, there has been a considerable amount of ingenuity spent on constructing formulæ for hæmin, but it must be confessed that as yet we are without a sure basis in the matter, since the authorities differ almost entirely in their views. It is clear that a good deal of slow accumulation of knowledge will have to take place before we are in a position to lay down the true constitution of hæmin, and the present papers represent a contribution to that task

It may be recalled that the hæmin molecule contains two carboxyl radicles, two imino-radicles, and an iron atom, in addition to numerous other groups of no direct importance here. When the iron atom is replaced by its equivalent in hydrogen, we obtain hæmatoporphorin.

If diazomethane is allowed to act on hæmatoporphorin, methylation occurs readily, but no analogous reaction takes place with hæmin itself. This evidently indicates some connexion between the presence or absence of the iron atom and the power of methylation.

Now if a hæmin derivative, known as β-bromohæmin, is esterified with ethyl alcohol, it yields β-bromoethylhæmin, and when diazomethane acts on the latter substance, β-methylethylhæmin is formed. In other words, the presence of the ethyl group is no hindrance to the further step of methylation. On the other hand, if β-chlorohæmin is allowed to react with diazomethane, β-chloromethylhæmin is produced, and on this compound diazomethane produces no further effect. In this instance, therefore, the introduction of the *methyl* group has inhibited further action. From this it follows that in esterification with ethyl alcohol and in methylation by diazomethane, two different groups are being attacked. Not only so, but the same difference is detected when the hæmin compound is esterified with ethyl alcohol and with

40 W. Küster, Zeitsch. physiol. Chem., 1917, 101, 25, 33, 43 ; A., i, 199, 200.

methyl alcohol: in the one case diazomethane reacts with the product, but in the case of the methyl ester there is no further methylation. From this evidence, Küster deduces that one of the carboxyl groups of hæmin is closely related to an imino-radicle (and hence to the iron atom, since the latter is supposed to be intimately connected in some way with the imino-group), and he suggests that the phenomena may be formulated somewhat as below:

$$\overset{\displaystyle\|}{CO \cdot O \cdot NH} \quad \text{MeOH} \quad \overset{\displaystyle\|}{CO \cdot O \cdot NH} \quad \xrightarrow{CH_2N_2} \quad \text{no further methylation}$$
$$\diagdown \qquad\qquad\qquad \diagdown$$
$$CO_2H \qquad\qquad\qquad CO_2Me$$

$$\overset{\displaystyle\|}{CO \cdot O \cdot NH} \quad \xrightarrow{\text{EtOH}} \quad \overset{\displaystyle\|}{CO \cdot O \cdot NEt} \quad \xrightarrow{CH_2N_2} \quad \overset{\displaystyle\|}{CO \cdot O \cdot NEt}$$
$$\diagdown \qquad\qquad\qquad \diagdown \qquad\qquad\qquad \diagdown$$
$$CO_2H \qquad\qquad\qquad CO_2H \qquad\qquad\qquad CO_2Me$$
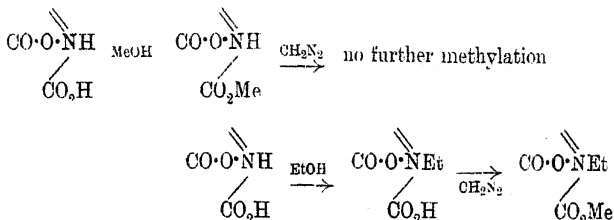
An attempt to support this by further evidence was made in the following way. When methyl alcohol acts on hæmin, methylhæmin is formed. The action of ethyl alcohol on this effects the displacement of the methyl by the ethyl group, yielding ethylhæmin. On the other hand, the direct action of ethyl alcohol on hæmin, since it involves the other carboxyl group, should yield an isomeric ethylhæmin. Hitherto, no such isomeric ethylhæmins have been isolated.

A. W. STEWART.

ANALYTICAL CHEMISTRY.

THE decrease in the number of papers which characterised this branch of chemistry last year has been still more pronounced during the past twelve months. As was to be expected, there have been relatively few contributions from German sources, whilst American journals have again been responsible for a large proportion of the published work.

Owing to the intensified shortage of materials, further attention has been given to the recovery of expensive reagents after use in analysis,[1] and to devising apparatus and methods for which cheaper or more available substances are required.

For example, an alloy of about 11 per cent. of platinum with 89 per cent. of gold has been used as a substitute for platinum for chemical apparatus,[2] and it has been shown that manna can replace glycerol in the titration of boric acid.[3]

Physical Methods.

Attention was directed in last year's Report[4] to certain sources of error in the methods of determining viscosity by means of the standard instruments, and to some of the suggestions which have been made to overcome these drawbacks. To obviate the effect of variations in the pressure due to the height of the column of liquid over the orifice, an apparatus has been constructed in which the liquid is driven at a definite temperature through the opening by means of measured centrifugal force, and the viscosity is expressed in terms of the acceleration due to gravity (g).[5]

In this connexion, mention may also be made of a modified form of "mercurial viscosimeter" intended for volatile liquids. In

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[1] B. Blount, *Analyst*, 1918, **43**, 119; *A.*, ii, 174.
[2] I. L. B. van der Marck, *Pharm. Weekblad*, 1918, **55**, 149. Compare *Ann. Report*, 1917, 146.
[3] L. E. Iles, *Analyst*, 1918, **43**, 323; *A.*, ii, 407.
[4] *Ann. Report*, 1917, 146.
[5] W. C. Cope, *J. Ind. Eng. Chem.*, 1917, **9**, 1046.

this instrument, an equal excess pressure is produced by means of an attachment above and below the column of liquid.[6]

There have been several further applications of the use of the spectroscope to analytical work. For example, a definite weight of a mineral containing a particular element is vaporised, and a screen in which is a horizontal slit is made to travel vertically at a measured velocity in front of the vapour. From the length of time during which a given ray of the element remains visible, the quantity of that element may be calculated.[7]

Another quantitative spectroscopic method has been used for the estimation of rubidium and cæsium in plant ash. The potassium, rubidium, and cæsium are separated as platinichlorides and converted into chlorides, and the solution is compared spectroscopically with standard solutions of the chlorides of the same elements prepared under the same conditions.[8]

An accurate means of titrating the acidity of coloured solutions has been based on the difference of the absorption spectra of certain indicators in acid and alkaline solutions. Equal quantities of an indicator are added to water and to the liquid under examination, and alkali is run in until the characteristic absorption band, observed with a pocket spectroscope, is seen in the same position in each case.[9]

The spectroscopic method affords a sensitive test for boron, being capable of detecting 1 part in 10,000.[10]

An optical method of estimating potassium and sodium has been based on the difference between the refractive indices of the respective chlorides in a 20 per cent. solution at 25°, that of sodium chloride being 1·36829, and that of potassium chloride 1·35992. Hence the relative proportion of the two salts in admixture may be calculated from the refractive index of the solution.[11]

It has also been shown that the refractive index may be used as one of the optical measurements for identifying cinchonine, cinchonidine, quinine, and quinidine when separated in crystalline form from a mixture of the four alkaloids. The refractive indices are determined in solutions of potassium mercuric iodide and glycerol, the optical refraction of which is known.[12]

For the estimation of malic and tartaric acids in the presence

[6] F. M. Lidstone, *J. Soc. Chem. Ind.*, 1918, **37**, 148T.

[7] A. B. P. Leme, *Compt. rend.*, 1918, **166**, 465 ; *A.*, ii, 172.

[8] W. O. Robinson, *J. Ind. Eng. Chem.*, 1918, **10**, 50 ; *A.*, ii, 132.

[9] A. Tingle, *J. Amer. Chem. Soc.*, 1918, **40**, 873 ; *A.*, ii, 236.

[10] A. de Gramont, *Compt. rend.*, 1918, **166**, 477 ; *A.*, ii, 173.

[11] B. A. Shippy and G. H. Burrows, *J. Amer. Chem. Soc.*, 1918, **40**, 185 ; *A.*, ii, 131.

[12] E. T. Wherry and E. Yanovsky, *ibid.*, 1063 ; *A.*, ii, 339.

of each other, advantage has been taken of the fact that the optical rotation of *l*-malic acid and of *d*-tartaric acid is increased by uranyl acetate, whereas the rotation of *l*-malic acid is reversed by ammonium molybdate. By plotting the optical rotations of each acid in solutions up to 1 per cent., in one case activated with uranyl acetate and in the other with ammonium heptamolybdate, two series of curves sloping in opposite directions are obtained. The points of intersection of each correlated pair of curves will show the amount of tartaric acid on the abscissæ and that of the malic acid on the ordinates.[13]

An optical method to which, of late years, increasing attention has been given is that termed nephelometry, or the measurement of the light reflected from a colloidal precipitate in suspension. Some of the principal technical applications of this method have been summarised, and the precautions necessary for obtaining trustworthy results with the nephelometer have been described. The method is useful for the estimation of precipitates of light colour, those of dark colour being more suitably measured colorimetrically. Substances which may conveniently be estimated in this way include nitrogen, phosphorus, calcium, fats, and proteins.[14]

The term "nephelometric value" is suggested as a convenient description of the amount of turbidity produced by a given quantity of a substance in a definite time in comparison with that produced by a standard substance under the same conditions. This value varies with the concentration of acid in the suspension and alters with the change of turbidity on keeping, but for each substance there is an optimum acid concentration which produces the greatest turbidity with the least change within a definite period of time.[15]

The detection of potassium by the flame test may be rendered much more sensitive by coating a glass plate with a gelatin film containing a mixture of two dyes, preferably Patent-blue and Tartrazine, in specified proportions. As seen through this screen, the potassium flame appears bright red with a border of yellowish-green. Only rubidium gives a flame of similar colour.[16]

A new application of a physical phenomenon as an indicator in acidimetry has been described. A measured quantity of a mixture of vaseline oil and oleic acid is made to issue from a jet just below the surface of the acid liquid, and the number of drops is counted.

[13] J. J. Willaman, *J. Amer. Chem. Soc.*, 1918, **40**, 693 ; *A.*, ii, 249.
[14] P. A. Kober, *J. Soc. Chem. Ind.*, 1918, **37**, 75T.
[15] F. A. Csonka, *J. Biol. Chem.*, 1918, **4**, 577 ; *A.*, ii, 277.
[16] A. Herzog, *Chem. Zeit.*, 1918, **42**, 145 ; *A.*, ii, 205.

On repeating this after successive additions of standard alkali, a sudden increase in the number of drops will be observed when neutrality is reached. The method thus depends on the measurement of the alteration in tension at the separation zone of two immiscible liquids.[17]

Gas Analysis.

The catalytic absorption of hydrogen from a mixture of gases by means of sodium oleate containing metallic nickel in suspension[18] cannot be recommended as an analytical process, since, apart from the difficulty of protecting the reagent from oxidation, the absorption of hydrogen is much too slow for quantitative work.[19]

A method of estimating benzene vapour in gases has been based on the increase in volume which occurs when a measured quantity of the gas is introduced into a special apparatus containing benzene vapour. By determining the increase in volume which would have been produced by gas free from benzene, the necessary data for the calculation are obtained.[20] Since, as a general rule, the vapour pressure of a liquid is independent of the nature of an inert gas above it, it is possible to estimate the amount of a vapour, such as benzene, toluene, or xylene, in a gas, such as air, by determining the difference between the pressure of the mixture and that of the same gas completely saturated with the vapour. For this purpose, two flasks are connected with a manometer, one of them containing the mixture, the pressure of which must be less than corresponds with complete saturation, and the other the gas by itself. Small bulbs containing the vapour are broken within each flask, and from the difference between the readings the pressure corresponding with the amount of vapour in the original mixture may be found.[21]

In using the "chlorate pipette"[22] for the absorption of hydrogen from gaseous mixtures, it is essential that all carbon monoxide should be removed, since otherwise the catalytic oxidation is retarded.[23] In the case of pure hydrogen, the "relative absorp-

[17] R. Dubrisay, *Ann. Chim.*, 1918, [ix], 9, 25; *A.*, ii, 368.

[18] E. Bosshard and E. Fischli, *Zeitsch. angew. Chem.*, 1915, 28, 365; *A.*, 1915, ii, 788.

[19] R. P. Anderson and M. H. Katz, *J. Ind. Eng. Chem.*, 1918, 10, 23; *A.*, ii, 124.   [20] R. P. Anderson, *ibid.*, 25; *A.*, ii, 84.

[21] H. S. Davis, M. D. Davis, and D. G. MacGregor, *ibid.*, 709, 712; *A.*, ii, 410, 411.

[22] K. A. Hofmann, *Ber.*, 1916, 49, 1650; *A.*, 1916, ii, 636.

[23] K. A. Hofmann and H. Schibsted, *ibid.*, 1663; *A.*, 1916, ii, 637.

tion velocity" is fairly constant, or increases slowly until half of the gas has been absorbed, whilst traces of carbon monoxide cause a rapid reduction in the rate of absorption. Hence, by using a standardised pipette and constructing a curve showing the rates of absorption up to this point (half-volume) with different minute quantities of carbon monoxide, it is possible to estimate the proportion of the latter in the gas.[24]

To obtain trustworthy results when using the Rayleigh interferometer in gas analysis, the gas chamber should be at least 1 metre in length, the gases compared must be at the same temperature and free from moisture, and the refractive index must be determined with great accuracy.[25]

Agricultural Analysis.

The dearth of potassium salts, mainly due to the stoppage of the German supplies, has caused attention to be directed to other possible sources of supply, such as félspar, dust from cement kilns, siliceous rocks, and the like. Hence the necessity for the accurate estimation of potassium is of paramount importance, and the various methods hitherto proposed have been subjected to critical examination during the past year.

There are little differences in the methods used for the extraction of soluble potassium salts from various materials, but in the case of substances, such as siliceous rocks, from which the potassium cannot be extracted by the citric acid process, various processes have been proposed. Trustworthy results are obtained by decomposing the material with pure hydrofluoric and sulphuric acids. After removal of iron, aluminium, manganese, and sulphuric acid, the alkalis are converted into chlorides, and the potassium is separated by the platinichloride or perchlorate method.[26] One objection to the hydrofluoric acid method is that very thorough washing is required to remove all potassium from the barium sulphate precipitate.[27] The Lawrence-Smith method, in which the material is heated with a mixture of calcium carbonate and ammonium chloride, then digested with water, freed from calcium, and the alkalis estimated in the filtrate, has the advantages of simplicity and of requiring reagents more readily obtainable than hydrofluoric acid in the pure condition, but, on the other hand,

[24] K. A. Hofmann and H. Schibsted, *Ber.*, 1918, **51**, 837; *A.*, ii, 329.

[25] F. M. Seibert and W. C. Harpster, *U.S. Bureau of Mines, Techn. Paper,* No. 185, 1918; *A.*, ii, 367.

[26] B. Blount, *Analyst*, 1918, **43**, 117; *A.*, ii, 174.

[27] G. N. Huntly, *ibid.*, 1918, **43**, 122.

it leaves about 1 per cent. of potassium unattacked, and a second treatment is required to decompose this.[28] If, however, the heating is continued for two hours at 170°, the decomposition is complete in one operation.[29] For the estimation of the potassium, the perchlorate method is quite trustworthy, although it is usually regarded as less accurate than the platinichloride method. The cobaltinitrite method is fairly satisfactory for materials containing 1 to 2 per cent. of potassium, but is liable to be erratic, and may yield too low results.[30] A gravimetric modification of the method which is suitable for the estimation of potassium in soils, fertilisers, etc., has been devised.[31] The method of calculating the proportions of potassium and sodium from the amount of chlorine in a weighed mixture of the chlorides has the drawbacks of most indirect methods. If the McLean-Van Slyke method is used for estimating the chlorine, the probable error in the amount of sodium increases with the decrease in the proportion of sodium to potassium, and is usually about 1 per cent.[32] In another indirect method, the potassium is calculated from the amount of platinum in the potassium platinichloride.[33]

The methods of estimating phosphoric acid in fertilisers, plant ash, etc., have been subjected to further critical examination during the year, and several new methods have been devised.[34] In one of these methods, intermediate precipitation of phosphoric acid as molybdate is avoided. The ash is dissolved in acetic acid, the calcium separated as oxalate, and the phosphoric acid precipitated as magnesium ammonium phosphate, citric acid being used to prevent the precipitation of iron and aluminium.[35] An analogous method has been recommended for the estimation of phosphoric acid in superphosphates.[36] Another method is to precipitate the phosphoric acid as a basic compound of mercury by the addition of yellow mercuric oxide, to decompose the latter with sodium sulphide, and to precipitate the phosphoric acid as ammonium magnesium phosphate.[37]

A precipitate of constant composition, $MgNH_4PO_4$, may be

[28] G. N. Huntly, *loc. cit.*

[29] P. Wenger and E. Brange, *Mon. Sci.*, 1918, [iv], **8**, *T.*, 97 ; *A.*, ii, 275.

[30] E. M. Hawkins, *Analyst*, 1918, **43**, 121.

[31] C. V. Garola and V. Braun, *Ann. Falsif.*, 1917, **10**, 572 ; *A.*, ii, 131.

[32] F. H. McCrudden and C. S. Sargent, *J. Biol. Chem.*, 1918, **33**, 235 ; *A.*, ii, 82.

[33] T. Steel, *Analyst*, 1918, **43**, 348 ; *A.*, ii, 407.

[34] Compare *Ann. Report*, 1917, 151.

[35] J. Grossfeld, *Zeitsch. anal. Chem.*, 1918, **57**, 28 ; *A.*, ii, 129. See also D. Balareff, *Zeitsch. anorg. Chem.*, 1918, **103**, 73 ; *A.*, ii, 332.

[36] G. Vortmann, *Zeitsch. anal. Chem.*, 1917, **56**, 465 ; *A.*, ii, 129.

[37] G. Vortmann, *loc. cit.*

obtained by causing ammonia to diffuse slowly into the acid solution containing magnesia and phosphoric acid in the presence of ammonium chloride. In Schultze's method of adding ammonia to the hot solution containing ammonium chloride. the precipitate which separates on cooling is not pure. A second solution and reprecipitation gives more trustworthy results.[38]

The presence of ammonia interferes with the accuracy of the results obtained by titrating the phosphomolybdic precipitate with standard alkali when phenolphthalein is used as indicator. This may be obviated by precipitating the phosphoric acid as potassium phosphomolybdate.[39] By adding a specified amount of ammonium nitrate to the solution before the addition of the ammonium molybdate. the precipitate will contain phosphoric oxide and ammonia in proportions corresponding with the triammonium compound, and the ammonia may be estimated by distillation with alkali and calculated into the corresponding amount of phosphoric acid.[40]

A method of estimating inositol-phosphoric acids in feeding-stuffs and the like has been described. It seems probable that inositol-pentaphosphoric acid. $C_6H_6(OH)(H_2PO_4)_5$, is the only inositol-phosphoric acid in the common feeding-stuffs.[41]

Ammonia in soil extracts may be estimated by Folin's aeration method, the extract being mixed with magnesium oxide and aerated in the cold for three hours. The ammonia is absorbed in acid towers, and the acid subsequently distilled with alkali. Before estimating nitric nitrogen in the extract, it is necessary to eliminate proteins, which yield ammonia when heated with sodium hydroxide. For this purpose, the liquid is treated with copper hydroxide and filtered. and the nitric nitrogen in the filtrate estimated by reduction with Devarda's alloy and distillation of the ammonia.[42]

A study of soil acidity and the hydrolytic ratio in soils has shown that there appears to be a definite relationship between the proportion of iron and aluminium compounds in a soil and its reaction towards litmus paper. In acid soils, the ratio

$$CaO : (Fe_2O_3 + Al_2O_3)$$
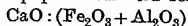
was found to exceed $1:1·3$, and the amount of lime required to neutralise such a soil may be found by calculating the quantity required to be added to the acid-soluble calcium oxide to bring the ratio to $1:1·3$.[43]

[38] D. Balareff, *Zeitsch. anorg. Chem.*, 1918, **104**, 53 ; *A.*, ii, 406.
[39] H. Heidenhain, *J. Ind. Eng. Chem.*, 1918, **14**, 436 ; *A.*, ii, 273.
[40] J. Clarens, *Compt. rend.*, 1918, **166**, 259 ; *A.*, ii, 128.
[41] J. B. Rather, *J. Amer. Chem. Soc.*, 1918, **40**, 523 ; *A.*, i, 212.
[42] B. S. Davisson, *J. Ind. Eng. Chem.*, 1918, **10**, 600 ; *A.*, ii, 370.
[43] C. H. Spurway, *J. Agric. Res.*, 1917, **11**, 659 ; *A.*, i, 152.

Organic Analysis.

Qualitative.—There have been few additions during the year to the methods of identifying groups of organic compounds. The principal new general method of examination has been based on the use of an acetic acid solution of chromic acid as an oxidising agent, which under specified conditions oxidises organic compounds with the liberation of acetone and aldehydes. These products may be separated by distillation and identified by conversion into their *p*-nitrophenylhydrazones, which are relatively insoluble. By means of this test, methylpentoses, such as rhamnose, may be identified in the presence of pentoses.[44]

It has been shown that the colour reaction given by lactic acid with thiophen and sulphuric acid is due to the formation of formaldehyde, and a sensitive test for aldehydes has been based on this fact. The shade of the red coloration given by aldehydes on treatment with an alcoholic solution of thiophen in the presence of concentrated sulphuric acid varies with the particular aldehyde. The test is capable of detecting 1 part of formaldehyde in 100,000.[45]

The guaiacol in guaiacol carbonate may be detected by giving a cherry-red coloration with ferric chloride and formaldehyde in the presence of sulphuric acid. Conversely, guaiacol carbonate may be used as a sensitive reagent for aldehydes in ethyl ether, being capable of detecting 1 part in 300,000.[46]

Attention is still being given to the sensitiveness of various methods of detecting hydrocyanic acid.[47] The only really distinctive test is that based on the formation of ferrocyanides, other reactions being less trustworthy, since they are also produced by other substances. In comparative tests with solutions of pure hydrocyanic acid, it was found that the following amounts of cyanogen (in mg. per litre) could be detected by the various methods: ferrocyanide 2, thiocyanate 0·1, picric acid 1, guaiacum 0·004, phenolphthalein 0·05, silver 0·03, and iodine–starch 0·1 mg.[48]

Formic acid may be detected by heating the liquid with a concentrated solution of sodium hydrogen sulphite, and, after cooling, pouring a dilute solution of sodium nitroprusside on to the surface. In the presence of formic acid, sodium hyposulphite is

[44] A. Windaus, *Zeitsch. physiol. Chem.*, 1917, **100**, 167 ; *A.*, ii, 22.

[45] W. R. Fearon, *Biochem. J.*, 1918, **12**, 179 ; *A.*, ii, 462.

[46] G. Maue, *Pharm. Zeit.*, 1918, **66**, 255 ; *A.*, ii, 336.

[47] Compare *Ann. Report*, 1916, 173 ; 1917, 153.

[48] I. M. Kolthoff, *Zeitsch. anal. Chem.*, 1918, **57**, 1 ; *A.*, ii, 138.

formed from the sodium hydrogen sulphite, and this reacts with the nitroprusside to produce a blue or green ring, due to the compound $Na_4Fe_2(CN)_6$, whilst hydrocyanic acid is liberated.[49]

A test for tartrates has been based on the solubility of cupric hydroxide in alkaline solutions of alkali tartrates. Although, by using potassium ferrocyanide for the detection of copper in the filtrate, this test is capable of detecting 0·2 milligram of tartrate, it cannot be regarded as distinctive, since other salts, including arsenites, borates, and phosphates, give a positive result in the absence of tartrates, whilst other compounds, including chromates, nitrites, and acetates, interfere with the reaction.[50]

A distinctive reaction for acetylcarbinol is produced by boiling its solution with *o*-aminobenzaldehyde, cooling the liquid, and treating it successively with acid and with excess of sodium hydrogen carbonate. A blue fluorescence is obtained, and, on extracting the liquid with ether and evaporating the extract, 3-hydroxy-2-methylquinoline is left as a white residue, which gives a red coloration with an alcoholic solution of ferric chloride.[51]

The formation of a yellow condensation product (m. p. 208°) with cinnamaldehyde enables malonic acid to be detected in the presence of oxalic, succinic, and citric acids. The drawback of the test is that about ten hours are required to form the condensation product, cinnamylidenemalonic acid.[52]

A sensitive reaction for mercury fulminate depends on the fact that it yields pararosaniline by heating with phenylhydrazine, subsequently diluting the liquid with alcohol, and adding a dilute acid.[53]

Ergotinine may be detected in an alcoholic solution containing 1 part in 1,240,000 by means of the potassium mercuric iodide reagent for alkaloids. Tanret's test for this alkaloid is rendered twice as sensitive by adding a trace of hydrogen peroxide as oxidising agent to the sulphuric acid.[54]

Quantitative.—It is perhaps in this division of analytical chemistry more than in any other that the reduced amount of research is indicated. There have been very few contributions to the methods of elementary analysis. In using cerium dioxide and cupric oxide as a catalyst in association with a mixture of lead peroxide and minium for a series of combustions of substances

[49] E. Comanducci, *Boll. Chim. farm.*, 1918, **57**, 101 ; *A.*, ii, 248.
[50] L. J. Curtman, A. Lewis, and B. R. Harris, *J. Amer. Chem. Soc.*, 1917, **39**, 2623 ; *A.*, ii, 87.
[51] O. Baudisch, *Biochem. Zeitsch.*, 1918, **89**, 279 ; *A.*, ii, 412.
[52] J. Bougault, *Ann. Chim. anal.*, 1918, **23**, 154 ; *A.*, ii, 413.
[53] A. Langhans, *Zeitsch. angew. Chem.*, 1918, **31**, i, 161 ; *A.*, ii, 414.
[54] L. Wolter, *Chem. Zeit.*, 1918, **42**, 446 ; *A.*, ii, 414.

containing nitrogen, it is essential to ensure complete decomposition of cupric nitrate after each combustion.[55]

In estimating nitrogen by Kjeldahl's method, the results are too low in the case of certain compounds, such as pyridine, piperidine, quinoline, and sometimes nicotine, possibly owing to the formation of sulphonic derivatives. To obtain accurate results for pyridine by the Arnold-Gunning modification, the heating should be continued for several hours after the solution has become clear.[56] The results obtained by Kjeldahl's method are too low when the decomposition has been effected by means of sulphuric acid and mercury, and to obviate this it is necessary to add zinc dust or potassium sulphide, followed by zinc turnings, prior to the distillation of the ammonia.[57]

A modification of Denigès's colorimetric method of estimating methyl alcohol has been described in which the liquid is oxidised by means of potassium permanganate, and the resulting formaldehyde is estimated by means of Schiff's reagent (magenta decolorised with sulphurous acid) under the same conditions as standard solutions of formaldehyde.[58]

A method of estimating formic acid has been based on its oxidation by means of chromic acid and measurement of the volume of carbon dioxide evolved in the reaction. Carbonates and oxalates, if present, are previously precipitated by means of calcium chloride, whilst acetates are not oxidised by chromic acid.[59] The methods of estimating the lower aliphatic acids have been critically examined, and a new method of separating acetic, propionic, and butyric acids has been based on the fact that light petroleum (b. p. 150° to 300°) will extract most of the butyric acid and some of the propionic acid from the solution after saturation with calcium chloride and the addition of a small amount of potassium chloride. The acidity of the original solution and of the petroleum fraction, and the weight of sodium salts, dried at 200°, obtained from both liquids, give the data for the calculation.[60] Butyric acid gives a red coloration when treated with hydrogen peroxide, ferrous ammonium sulphate, and sulphuric acid, and then with sodium hydroxide solution, sodium nitroprusside, and a slight excess of acetic acid. This colour reaction has been made the basis of a colorimetric method of estimating butyric acid.[61]

[55] H. L. Fisher and A. H. Wright, *J. Amer. Chem. Soc.*, 1918, **48**, 868.
[56] H. C. Brill and F. Agcaoili, *Philippine J. Sci.*, 1917, **12**A, 261 ; *A.*, ii, 172.
[57] E. Salm and S. Prager, *Chem. Zeit.*, 1918, **42**, 104 ; *A.*, ii, 173.
[58] T. von Fellenberg, *Biochem. Zeitsch.*, 1918, **85**, 45 ; *A.*, ii, 177.
[59] F. Tsiropinas, *J. Ind. Eng. Chem.*, 1917, **9**, 1110 ; *A.*, ii, 137.
[60] R. D. Crowell, *J. Amer. Chem. Soc.*, 1918, **40**, 453 ; *A.*, ii, 137.
[61] G. Denigès, *Ann. Chim. anal.*, 1918, **23**, 27 ; *A.*, ii, 138.

For the separation of oxalic acid from tartaric acid, the solution is treated with a sufficient quantity of boric acid to prevent the precipitation of calcium tartrate, and the oxalic acid precipitated as calcium oxalate. The precipitate is washed and ignited, and the resulting calcium oxide titrated with standard hydrochloric acid.[62]

A comparative study of the methods of estimating acetone has shown that Messenger's method, which depends on the formation of iodoform, gives incorrect results, whilst no improvement is effected by substituting arsenious acid for thiosulphate in the titration. Kebler's modification of Robineau and Rollin's method[63] has been found the most trustworthy.[64]

The work done in connexion with the subject of oils and fats has been mainly concerned with the characteristics of individual fats, and few new methods of analysis have been introduced. For example, the composition of butter fat has been once more investigated by modern methods, including esterification, with results differing considerably from those previously recorded.[65]

The measurement of the optical dispersion of oils from an analytical point of view has been studied, and it has been found that most of the common oils have very similar dispersions (0·0186 to 0·0207), with the exception of coconut oil (0·0167) and tung oil (0·0371).[66]

A method of detecting foreign fats in butter has been based on a fractionation of the glycerides by treatment with a mixture of two solvents (for example, alcohol and ether), one of which is more volatile and dissolves fat more readily than the other. A current of air is passed through the solution to evaporate the more volatile solvent, and the less readily soluble glycerides which separate at a certain stage during the evaporation are examined.[67]

Twitchell's method of estimating resin in soap is not applicable to resins other than colophony, and has the drawback that it causes pure fatty acids to show an apparent resin content. These objections are obviated by a method based on the fact that nitrated resins are insoluble in light petroleum, whilst the fatty acids after the nitration may be quantitatively separated from the solution.[68]

In estimating citral by Hiltner's colorimetric method, certain

[62] A. Bau, *Chem. Zeit.*, 1918, **42**, 425 ; *A.*, ii, 412.

[63] *J. Amer. Chem. Soc.*, 1897, **19**, 316 ; *A.*, 1898, ii, 56.

[64] A. J. Field, *J. Ind. Eng. Chem.*, 1918, **10**, 552 ; *A.*, ii, 377.

[65] E. B. Holland and J. P. Buckley, jun., *J. Agric. Res.*, 1918, **12**, 719 ; *A.*, ii, 250.

[66] P. J. Fryer and F. E. Weston, *Analyst*, 1918, **43**, 311.

[67] A. Seidenberg, *J. Ind. Eng. Chem.*, 1918, **10**, 627.

[68] V. Fortini, *Annali Chim. Appl.*, 1918, **9**, 102.

kinds of orange and lemon oils give a blue or green coloration instead of the usual yellow tint when treated with *m*-phenylene-diamine hydrochloride. This may be prevented by adding oxalic acid to the reagent.[69]

Several additions have been made to the methods of sugar analysis. For the estimation of lævulose in the presence of aldoses, the clarified solution is inverted by the Clerget-Herzfeld method, cooled, and treated with bromine in a proportion corresponding with the amount of aldoses. Only the aldoses are oxidised, and the lævulose may subsequently be estimated by determining its reducing power.[70] A modification of Bougault's iodometric method[71] is described in which a solution containing sodium phosphate and hydroxide takes the place of the sodium carbonate solution.[72]

Another iodometric method of estimating dextrose consists in treating the solution with about twice the amount of standard iodine solution required to oxidise the dextrose to gluconic acid,

$$C_6H_{12}O_6 + I_2 + 3NaOH = 2NaI + 2H_2O + HO \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CO_2Na,$$

and then with an excess of sodium hydroxide. After twelve to twenty minutes, the solution is made slightly acid and the excess of iodine titrated. Ketoses and sucrose do not affect the results, and the method may therefore be used for estimating aldoses in the presence of other sugars.[73]

The proportion of lactose in admixture with sucrose and invert-sugar may be calculated from the determination of the polarisation and reducing power of the mixture under standard conditions by means of an empirical formula constructed from data obtained with mixtures of the pure sugars.[74]

A method of estimating phenol in the presence of the three cresols is based on the determination of the specific gravity and solidifying point of the mixture, the necessary data for the equation having been obtained empirically from the results given by mixtures of the pure substances.[75]

The drawback of Dowzard's colorimetric method of estimating brucine in presence of strychnine[76] is that the coloration fades with varying velocity. The method may be rendered more trustworthy

[69] C. E. Parker and R. S. Hiltner, *J. Ind. Eng. Chem.*, 1918, **10**, 608; *A.*, ii, 377.

[70] Herzfeld and Lenart, *Zentr. Zuckerind.*, 1918, **68**, 227.

[71] Compare *Ann. Report*, 1917, 159.

[72] H. Colin and O. Liévin, *Bull. Soc. chim.*, 1918, [iv], **23**, 403; *A.*, ii, 461.

[73] R. Willstätter and G. Schudel, *Ber.*, 1918, **31**, 780; *A.*, ii, 337.

[74] J. Grossfeld, *Zeitsch. Nahr. Genussm.*, 1918, **35**, 249; *A.*, ii, 337.

[75] G. W. Knight, C. T. Lincoln, G. Formanek and H. L. Follett, *J. Ind. Eng. Chem.*, 1918, **10**, 9; *A.*, ii, 84.   [76] *P.*, 1902, **18**, 220.

by using a mixture of concentrated nitric and 20 per cent. sulphuric acids, and adding a saturated solution of potassium chlorate immediately after the reaction.[77]

Theobromine may conveniently be estimated by converting it into its periodide, $C_7H_8O_2N_4,HI,I_4$ and titrating the excess of iodine. The method is applicable in the presence of sodium acetate or salicylate.[78]

Pyridine or pyridine bases in ammonium salts or ammonia solution may be estimated by precipitation with iodine in excess from a solution acidified with sulphuric acid. The excess of iodine is removed by means of thiosulphate, and the periodides are titrated with standard alkali, first with methyl-orange and then with phenolphthalein as indicator. The amount of pyridine sulphate is calculated from the difference between the two titrations. The sensitiveness of the method and completeness of the precipitation are increased by adding sodium chloride to the solution.[79]

Abnormal results are sometimes obtained by Sörensen's method of formaldehyde titration for amino-acids, polypeptides, etc. This has been shown to be usually due to the presence of an imino-group, which is not converted by formaldehyde into a neutral group, as in the case of simple amino-acids, but into a group which is still somewhat basic, and so causes too low results.[80]

Inorganic Analysis.

Qualitative.—Further applications of the use of textile fibres impregnated with reagents in microscopical qualitative analysis have been devised.[81] It has been shown that the difficulties which attend the use of test papers are obviated when a single test fibre is used. For example, a fibre of turmeric viscose silk is a sensitive reagent for boric acid, being capable of detecting 0·000025 milligram of boron, whilst wool fibres saturated with zinc sulphide are suitable for the detection of traces of copper (0·001 milligram) and other heavy metals.[82]

A test for iodides in the presence of cyanides has been based on the precipitation of the cyanide by means of cobalt nitrate, and

[77] A. Wöber, *Zeitsch. angew. Chem.*, 1918, **31**, i, 124 ; *A.*, ii, 339.

[78] W. O. Emery and G. C. Spencer, *J. Ind. Eng. Chem.*, 1918, **10**, 605 ; *A.*, ii, 380.

[79] T. F. Harvey and C. F. Sparks, *J. Soc. Chem. Ind.*, 1918, **37**, 41T.

[80] S. L. Jodidi, *J. Amer. Chem. Soc.*, 1918, **40**, 1031 ; *A.*, ii, 379.

[81] Compare E. M. Chamot and H. I. Cole, *J. Ind. Eng. Chem.*, 1917, **9**, 969 ; *A.*, 1917, ii, 576.

[82] E. M. Chamot and H. I. Cole, *ibid.*, 1918, **10**, 48 ; *A.*, ii. 129.

detection of the iodide in the filtrate by oxidation with potassium permanganate in the presence of sulphuric acid and chloroform. Comparative experiments with different oxidising agents have shown that the liberation of iodine from potassium iodide is least affected by cyanides when permanganate is used as the oxidising agent.[83]

A solution of mercuric nitrate in nitric acid may be used for the detection of the sulphuric ion in insoluble sulphates. This reagent forms turpeth mineral, which may readily be identified under the microscope. In the case of mixtures, the sulphate should be precipitated as barium sulphate, and the test applied to the precipitate.[84]

A method of detecting selenium in sulphuric acid depends on the fact that such acid shows a pronounced violet coloration when tested with aspidospermine. Sulphuric acid free from selenium does not show this reaction, but after the addition of an oxidising agent produces a rose-red coloration.[85]

The detection of phosphoric acid by means of molybdic acid solution is rendered ten times more sensitive by the addition of pyridine to the reagent.[86]

The compounds formed on adding a concentrated solution of potassium iodide to ammoniacal solutions of cadmium and nickel salts afford a means of separating and identifying those metals in presence of other metals. Cadmium forms an insoluble, white precipitate, $Cd(NH_3)_2I_2$, composed of white octahedra, whereas copper gives no precipitate with the reagent. The nickel compound is bluish-violet, has the formula $Ni(NH_3)_6I_2$, and is also composed of regular octahedra. Cobalt forms an analogous precipitate, and should therefore be separated before applying the test for nickel.[87]

On heating for a few minutes a solution containing osmium in the tetroxide condition, or an osmichloride, with an excess of thiocarbamide and a few drops of hydrochloric acid, a coloration is obtained ranging from rose to deep red, according to the concentration of the osmium. The reaction, which is capable of detecting 1 part of osmium in 100,000, is due to the formation of a red compound of the composition $[Os6NH_2 \cdot CS \cdot NH_2]Cl_3, H_2O$.[88]

Other colour reactions which have been described are those given by thorium and zirconium with an aqueous solution of pyrogallol-

[83] L. J. Curtman and C. Kaufman, *J. Amer. Chem. Soc.*, 1918, **40**, 914; *A.*, ii, 272.

[84] G. Denigès, *Bull. Soc. chim.*, 1918, [iv], **23**, 36; *A.*, ii, 82.

[85] L. P. J. Palet, *Anal. Soc. Quím. Argentina*, 1917, **5**, 121; *A.*, ii, 127.

[86] G. Vortmann, *Zeitsch. anal. Chem.*, 1917, **56**, 465; *A.*, ii, 129.

[87] A. Agrestini, *Gazzetta*, 1918, **48**, ii, 30; *A.*, ii, 455.

[88] L. A. Tschugaev, *Compt. rend.*, 1918, **167**, 235; *A.*, ii, 335.

aldehyde. This reagent gives a yellow coloration and precipitate with thorium salts, whilst with zirconium compounds it produces a similar coloration and precipitate after boiling or the addition of hydrogen peroxide. The test is capable of detecting 0·1 milligram of thorium nitrate in 100 c.c. The reaction is not produced by pyrogallol, pyrogallolcarboxylic acid, or protocatechualdehyde.[89]

Quantitative.—The use of thymolsulphophthalein as an indicator in acidimetric titrations has many advantages, owing to the fact that it shows two distinct changes of colour at different hydrion concentrations. It may therefore be used for the differential titration of mixtures of weak and strong acids, such as benzoic and hydrochloric acids, or acetic and sulphuric acids, although in the latter case the error may be as much as ±0·5 per cent. Another application of this indicator is in the titration of aniline with hydrochloric acid.[90]

In titrating free hydrochloric acid in gastric juice, using dimethylaminoazobenzene, Congo-red, or tropæolin as indicator, the presence of large amounts of organic acids, or of hydrochloric acid in a state of loose combination, renders the results uncertain. This may be obviated by adding alcohol to prevent the dissociation of organic acids, and thus suppress their acid properties towards the indicators.[91]

The alkalinity of very dilute solutions ($N/10,000$ to $N/40,000$) may be estimated by means of an iodotannic reagent consisting of a mixture of $N/10$-iodine solution and 1 per cent. tannin solution. The alkaline solution is run into 2 c.c. of the reagent until a distinct red colour appears, after which it is gradually introduced, and a drop of the mixture tested with starch-paper after each addition until a blue colour is no longer produced.[92]

A method of estimating the alkalinity of certain liquids, such as soap solutions, has been based on the measurement of the volume of nitrogen which the solution liberates from a nitrosoamine. This gives results sufficiently trustworthy ·for practical purposes, although not so accurate as those obtained by measuring the pressure of the gas. Nitrosotriacetonamine and nitrosovinyldiacetonamine are suitable compounds for titrations within definite limits of hydroxyl-ion concentration.[93]

An acidimetric method of titrating zinc will be found of use

[89] H. Kaserer, *Chem. Zeit.*, 1918, **42**, 170 ; *A.*, ii, 244.

[90] A. B. Clark and H. A Lubs, *J. Amer. Chem. Soc.*, 1918, **40**, 1443 ; *A.*, ii, 449.

[91] G. Kelling, *Berlin. Klin. Woch.*, 1918, **54**, 334 ; *A.*, ii, 450.

[92] D. E. Tsakalotos and D. Dalmas, *Bull. Soc. chim.*, 1918, [iv], **23**, 391 ; *A.*, ii, 454.

[93] F. Francis, *J. Soc. Chem. Ind.*, 1918, **37**, 252T.

when a rapid estimation of the metal is required. The solution, which must contain the zinc in the form of chloride and be free from other heavy metals, is neutralised with sodium hydroxide, methyl-orange being used as indicator, and, after the addition of phenolphthalein, is titrated with $N/10$-sodium hydroxide solution. The end-point of the titration is indicated by the pink colour not disappearing when the liquid is boiled. The precipitated zinc hydroxide does not interfere with the accuracy of the results.[94]

Several new iodometric methods have been published during the year. For the estimation of copper and iron, advantage has been taken of the fact that the salts of both metals liberate iodine from a solution of potassium iodide in dilute acetic acid. When both iron and copper are present, the former may be precipitated as ferric phosphate, which does not liberate iodine from potassium iodide, and the liquid again titrated. The iodine found in the first titration is equivalent to the copper and iron together, whilst that obtained in the second titration corresponds with the amount of copper. The method is also applicable in the presence of zinc and aluminium.[95]

In another iodometric method of estimating copper, the solution of the metal is nearly neutralised, and the copper converted into cupric acetate. After the addition of excess of sodium thiosulphate and slight excess of potassium thiocyanate, the liquid is filtered from the cuprous thiocyanate, and the excess of thiosulphate in the filtrate titrated with standard iodine solution. Of the common metals, only iron interferes with the estimation.[96]

In estimating sulphites by oxidation to sulphates by means of potassium iodate, it is essential that there should be an excess of the iodate and sufficient hydrochloric acid to prevent the hydrolysis of the iodine chloride formed in the reaction

$$H_2S + 2KIO_3 + 4HCl = 2ICl + H_2SO_4 + 2H_2O + 2KCl.$$
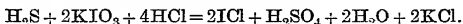
The excess of iodate is then estimated by means of standard iodine solution. The method may also be used for estimating lead sulphide, which is introduced in a freshly precipitated state into the iodate solution.[97]

In estimating selenious acid by the direct process, it is necessary to add four times the theoretical amount of potassium iodide, to heat the mixture with hydrochloric acid in a distillation flask, and to titrate the iodine both in the receiver and the residue. The

[94] R. Howden, *Chem. News*, 1918, **117**, 322 ; *A.*, ii, 408.
[95] H. Ley, *Chem. Zeit.*, 1917, **41**, 763 ; *A.*, ii, 21.
[96] J. Moir, *Chem. News*, 1918, **117**, 133 ; *A.*, ii, 83.
[97] R. S. Dean, *J. Amer. Chem. Soc.*, 1918, **40**, 619 ; *A.*, ii, 204.

indirect method [98] is also trustworthy when a similar procedure is used. Selenic acid is best estimated by reduction with hydriodic acid.[99]

In analysing a mixture of phosphorous, hypophosphorous, and phosphoric acids, the phosphorous acid may first be estimated by determining the iodine absorption of the solution. The hypophosphorous acid is then hydrolysed in the presence of hydrochloric acid in accordance with the equation $H_4P_2O_6 + H_2O = H_3PO_3 + H_3PO_4$, and the resulting phosphorous acid estimated iodometrically as before. Finally, the solution is oxidised and the total phosphoric acid estimated [1]

For the estimation of hypobromite in the presence of bromate or hypoiodite in the presence of iodate, the hypobromite or hypoiodite is oxidised by means of a mixture of sodium hydroxide and hydrogen peroxide, $NaBrO + H_2O_2 = NaBr + H_2O + O_2$, the liquid boiled to expel the excess of hydrogen peroxide, potassium iodide and sulphuric acid are added, and the iodine liberated by the bromate is titrated. Another portion of the solution is treated with potassium iodide and sulphuric acid to obtain the iodine equivalent of the hypobromite and bromate together, and the hypobromite is obtained by difference.[2] A method of estimating iodates and bromates in the same solution has been based on the fact that bromates are gradually decomposed by dilute hydrochloric acid, with the formation of hydrobromic acid and hypochlorous acid, whilst iodates are not affected. The iodine equivalent of the two compounds together is obtained as described above. Another portion of the solution is then treated with dilute hydrochloric acid, and subsequently oxidised with hydrogen peroxide and sodium hydroxide, and the iodine equivalent again determined. The difference between the amounts obtained in the two titrations corresponds with the bromate.[3]

An iodometric method of estimating nitrites has been based on the reaction $NaNO_2 + 2HI = NaI + I + NO + H_2O$, which is carried out in a series of connected flasks. The liberated iodine is titrated with arsenious acid.[4]

In this connexion, mention may also be made of a general method of estimating iodine in inorganic and organic compounds, based on

[98] F. A. Gooch and A. W. Peirce, *Zeitsch. anorg. Chem.*, 1896, **11**, 249; *A.*, 1896. ii, 334.

[99] L. Moser and W. Prinz, *Zeitsch. anal. Chem.*, 1918, **57**, 277; *A.*, ii, 451.

[1] R. G. van Name and W. J. Huff, *Amer. J. Sci.*, 1918, [iv], **45**, 91; *A.*, ii, 128.

[2] E. Rupp, *Zeitsch. anal. Chem.*, 1918, **57**, 16; *A.*, ii, 125.

[3] E. Rupp, *ibid.*, 19; *A.*, ii. 126.

[4] F. Dienert, *Compt. rend.*, 1918, **167**, 366; *A.*, ii, 370.

its conversion into iodine trichloride. The iodine liberated in the reaction, $6FeSO_4 + 3H_2SO_4 + 2ICl_3 = 3Fe_2(SO_4)_3 + 2I + 6HCl$, is extracted with chloroform and titrated with thiosulphate solution.[5]

An oxidimetric method of estimating thorium has been described. The thorium is precipitated as oxalate, and the precipitate heated at 85° with dilute sulphuric acid, and titrated first in the cold and finally at 85° with standard potassium permanganate solution. If a known excess of oxalic acid has been used for the precipitation, the filtrate may be heated to 85° and titrated with permanganate.[6] An extension of the method may also be used for estimating fluorine. The fluoride is precipitated as thorium fluoride by means of an excess of thorium, the excess of which, in turn, is precipitated as thorium oxalate.[7]

Metallic silver may be used as a reducing agent in the volumetric estimation of iron, the dissolved silver being subsequently precipitated as thiocyanate. The filtrate is treated with an excess of silver nitrate and titrated with potassium permanganate solution. The presence of titanium does not affect the results, but vanadium is quantitatively reduced by silver.[8] Titanous chloride may also be used as a reducing agent for ferric salts, the excess being subsequently removed by means of copper sulphate.[9]

It has been pointed out that in titrating potassium permanganate solution containing nitric acid with sodium arsenite, the latter has a reducing value considerably in excess of that shown when no acid is present. It is probable that a manganic compound is formed under these conditions.[10]

In estimating vanadium and molybdenum volumetrically by means of titanous chloride,[11] the addition of the indicator, potassium thiocyanate, before the titanous chloride causes the vanadic acid to be reduced first. Advantage may be taken of this fact in the analysis of steel, the vanadium and molybdenum being first estimated together as described (loc. cit.), and the vanadium then separately titrated after the addition of thiocyanate.[12]

To obtain trustworthy results in the titration of chlorides by Volhard's method, the liquid should be stirred at the first indica-

[5] N. Tarugi, *Gazzetta*, 1918, **48**, ii, 1 ; *A.*, ii, 203.

[6] F. A. Gooch and M. Kobayashi, *Amer. J. Sci.*, 1918, [iv], **45**, 227 ; *A.*, ii, 177.

[7] *Ibid.*, 370 ; *A.*, ii, 239.

[8] G. Edgar and A. R. Kemp, *J. Amer. Chem. Soc.*, 1918, **40**, 777 ; *A.*, ii, 242.

[9] L. Brandt, *Chem. Zeit.*, 1918, **42**, 433, 450 ; *A.*, ii, 409.

[10] F. Ibbotson, *Chem. News*, 1918, **117**, 157 ; *A.*, ii, 175.

[11] A. Travers, *Compt. rend.*, 1917, **165**, 362 ; *A.*, 1917, ii, 545 ; *Ann. Report*, 1917, 165.   [12] A. Travers, *ibid.*, 1918, **166**, 289 ; *A.*, ii, 135.

tion of change of colour, and the titration then completed. Thiocyanates, if present, should be oxidised with sodium peroxide in sulphuric acid solution before the titration.[13] In using the method conversely for the estimation of silver, the presence of other metals, such as mercury, lead, nickel, or cobalt, or of lower oxides of nitrogen, causes the results to be inaccurate. The use of palladious iodide as indicator renders the method more trustworthy and sensitive and capable of being used in the presence of the substances mentioned. The addition of a small amount of gum arabic is advisable to prevent the precipitation of silver or palladious iodide during the titration.[14]

A volumetric method of estimating chlorides, bromides, and cyanogen consists in titrating the solution with standard mercuric nitrate solution, using sodium nitroprusside as indicator. The results are more accurate than those obtained by Volhard's method, and the method can be used in the presence of sulphates and phosphates, although sulphites and nitrites must be removed before the titration. Conversely, the method is applicable to the estimation of mercury.[15]

The presence of dissolved or gelatinous silica does not interfere with the titration of chlorine with silver nitrate, provided that the liquid is made neutral to phenolphthalein with nitric acid, and any resulting gelatinous mass is finely distributed throughout the liquid before introducing the reagent.[16]

One objection to the method of titrating copper with potassium cyanide solution is that the end-point of the reaction is no longer sharp when much less than 1 gram of copper per litre is present. For smaller quantities, a volumetric method has been based on the fact that a solution of a double carbonate of copper and an alkali metal in excess of sodium carbonate solution gives a sharp reaction with potassium cyanide. The double carbonate is prepared by adding a solution of sodium carbonate and sodium hydrogen carbonate to the copper solution.[17]

The results obtained by the volumetric method of estimating lead by means of ammonium molybdate, as ordinarily used, are too high. To obviate this, it is essential to dissolve the lead sulphate in the smallest possible quantity of ammonium acetate solution.[18]

Calcium may be estimated volumetrically by precipitating it under specified conditions with an excess of ammonium oxalate,

[13] I. M. Kolthoff, *Zeitsch. anal. Chem.*, 1917, **56**, 568; *A.*, ii, 124.
[14] L. Schneider, *J. Amer. Chem. Soc.*, 1918, **40**, 583; *A.*, ii, 205.
[15] E. Votoček, *Chem. Zeit.*, 1918, **42**, 257; *A.*, ii, 238.
[16] G. Bruhns, *Zeitsch. angew. Chem.*, 1918, **31**, i, 156; *A.*, ii, 368.
[17] M. P. Applebey and K. W. Lane, *Analyst*, 1918, **43**, 268; *A.*, ii, 276.
[18] Lindt, *Zeitsch. anal. Chem.*, 1918, **57**, 71; *A.*, ii, 242.

the excess of which is subsequently titrated in the filtrate by mean of potassium permanganate solution.[19]

Turning to the gravimetric methods, it will be found that several new methods of separating metals in different groups have been described. For example, for the separation of copper, zinc, cadmium, nickel, and cobalt, the metals are precipitated by means of sodium carbonate, the precipitate is dissolved in the minimum quantity of ammonia solution, and the liquid diluted and boiled until reprecipitation is complete. The precipitate may be an oxide, as in the case of copper, a hydroxide or hydrocarbonate, as in the case of zinc and nickel, or a carbonate, as cadmium carbonate. The precipitate is ignited, or sometimes is preferably reduced with hydrogen, and the metal weighed. For the separation of individual metals, modifications of various well-known methods may be employed.[20]

Another new method is concerned with the separation of metals of the copper group from those of the arsenic group. It is based on the facts that the sulphides of mercury, arsenic, antimony, and tin are soluble in a solution of sodium hydroxide saturated with hydrogen sulphide, and then mixed with a more concentrated sodium hydroxide solution, whereas the sulphides of lead, bismuth, copper, and cadmium are insoluble therein.[21]

Dicyanodiamide sulphate is a convenient reagent to use for the quantitative precipitation of copper or nickel when it is desirable not to use an alkali hydroxide. It may also be used as a group reagent for separating copper and nickel from zinc, aluminium, arsenic, lead, and antimony.[22]

The use of hydrofluoric acid in electrochemical analysis is mentioned elsewhere.[23] A further application of this reagent has been based on the fact that stannic tin and tungsten are not precipitated by hydrogen sulphide from an acidified fluoride solution, and may thus be separated from copper, lead, silver, mercury, antimony, and arsenic.[24]

The accuracy of the results obtained by estimating sulphuric acid as barium sulphate depends to a considerable extent on the rate at which the barium chloride is added, whilst other factors, such as the concentration, the amount of stirring, and the acidity of the liquid have a much smaller influence. At least one and a-half

[19] J. Grossfeld, *Chem. Zeit.*, 1917, **41**, 842; *A.*, ii, 83.

[20] A. Carnot, *Compt. rend.*, 1918, **166**, 245, 329; *A.*, ii, 133.

[21] M. C. Sneed, *J. Amer. Chem. Soc.*, 1918, **40**, 187; *A.*, ii, 133.

[22] H. Grossmann and J. Mannheim, *Chem. Zeit.*, 1918, **42**, 17; *A.*, ii, 175.

[23] See p. 140.

[24] N. H. Furman, *J. Amer. Chem. Soc.*, 1918, **40**, 895; *A.*, ii, 277.

minutes should be allowed for the addition of the reagent. In the presence of potassium salts, the results are too low, but tend to compensate the high results caused by a too rapid addition of barium chloride.[25]

Gravimetric methods of estimating chromates and dichromates as barium chromate and as silver chromate have been described. In each case, the insoluble chromates are precipitated and washed under specified conditions, dried at 132°, and weighed. The silver method is the more trustworthy, but is not applicable in the presence of chlorides, whilst the barium method cannot be used in the presence of sulphates. Nitrates, chlorates, and acetates do not affect the results, but even when the silver method is used, sulphates cause the results to be too high.[26]

A similar method has been devised for the estimation of strontium, which is precipitated as sulphate, carbonate, or oxalate, preferably the last. In each case, the precipitate is washed with a saturated solution of the respective strontium salt, dried at 132°, and weighed. It should be noted that magnesium chloride interferes with the estimation as oxalate.[27] For the separation and estimation of barium when associated with strontium, the saturated solution of the two chlorides is treated with a mixture of hydrochloric acid and ether, and the precipitated barium chloride washed with the same mixture, dried at 150°, and weighed.[28]

For the estimation of magnesium, the compound

$$MgNH_4PO_4,6H_2O$$

is precipitated at 90°, washed with ammonia and methyl alcohol, dried over calcium chloride, and weighed. The method cannot be used, however, when any considerable quantity of potassium chloride or sodium chloride is present.[29]

Several new methods of separation by means of volatilisation have been published. When tantalum is precipitated as tantalic acid, the silica which is usually present cannot be separated by treatment with hydrofluoric acid without some loss of tantalum. To obviate this difficulty, the tantalic acid may be volatilised in a current of hydrogen chloride at 900°, and the residual silica weighed.[30]

Other volatilisation methods have been devised for vanadium,

[25] Z. Karaoglanow, *Zeitsch. anal. Chem.*, 1917, **56**, 417; 1918, **57**, 77; *A.*, ii, 47, 239. *Zeitsch. angew. Chem.*, 1918, **31**, i, 160; *A.*, ii, 369.

[26] L. W. Winkler, *Zeitsch. angew. Chem.*, 1918, **31**, i, 46; *A.*, ii, 176.

[27] *Ibid.*, 80, 83; *A.*, ii, 241.

[28] F. A. Gooch and M. A. Soderman, *Amer. J. Sci.*, 1918, [iv], **46**, 538; *A.*, ii, 408.

[29] L. W. Winkler, *Zeitsch. angew. Chem.*, 1918, **31**, i, 211; *A.*, ii, 455.

[30] A. Travers, *Compt. rend.*, 1918, **166**, 491; *A.*, ii, 177.

molybdenum, and tungstic acid. In the case of vanadium, the compound is heated in a current of carbon dioxide and carbon tetrachloride in a silica tube, and the resulting vanadium chlorides collected in dilute nitric acid and water. The vanadic acid is then reduced to vanadyl sulphate, and the solution titrated with standard permanganate solution.[31] Molybdenum compounds are volatilised at 400—560° in carbon tetrachloride vapour, and the volatilised molybdic acid is collected, evaporated with nitric acid, and weighed.[32] For the volatilisation of tungstic acid, a current of carbon dioxide saturated with carbon tetrachloride vapour is used, and the separated acid treated as in the case of molybdic acid.[33]

The new colorimetric methods include one for the estimation of manganese, which depends on the oxidation of manganese salts by means of an alkali periodate in acid solution, and comparison of the resulting permanganate with standard solutions.[34] Tungstic acid may also be estimated colorimetrically by reducing it by means of titanous chloride, and comparing the blue oxide which remains in suspension under certain conditions with standard suspensions of known composition. The method is not applicable in the presence of vanadium, phosphorus, or molybdenum, and these if present must be removed prior to the estimation.[35]

Electrochemical Analysis.

Further applications of the electrometric method of titration[36] have been described during the year. For example, it is a convenient method of estimating manganese in steel. For this purpose, the manganese is oxidised to permanganate by means of sodium bismuthate or ammonium persulphate, and the resulting solution titrated with mercurous nitrate solution. The presence of chromates or vanadates does not interfere with the estimation.[37] Another modification of the method has been devised for the titration of solutions containing proteins, a special apparatus being used to prevent local reactions when the reagent first comes in contact with the solution.[38]

[31] P. Jannasch and H. E. Harwood, *J. pr. Chem.*, 1918, [ii], **97**, 93 ; *A.*, ii, 373.   [32] P. Jannasch and O. Laubi, *ibid.*, 154 : *A.*, ii, 489.

[33] P. Jannasch and R. Leiste, *ibid.*, 141 ; *A.*, ii, 460.

[34] H. H. Willard and L. H. Greathouse, *J. Amer. Chem. Soc.*, 1917, **39**, 2366 ; *A.*, ii, 84.

[35] A. Travers, *Compt. rend.*, 1918, **166**, 416 ; *A.*, ii, 176.

[36] Compare *Ann. Report*, 1917, 166.

[37] G. L. Kelley, M. G. Spencer, C. B. Illingworth, and T. Gray, *J. Ind. Eng. Chem.*, 1918, **10**, 19 ; *A.*, ii, 134.

[38] J. C. Baker and L. L. Van Slyke, *J. Biol. Chem.*, 1918, **35**, 137 ; *A.*, ii, 380.

On titrating oxalic acid with sodium hydroxide solution, a sharp change occurs in the electrical conductivity of the liquid at the moment when the first hydrogen atom is displaced by sodium. Should, however, the sodium hydroxide contain carbonates, the results obtained in the estimation of oxalic acid will be too high. By means of this method, it is also possible to titrate strong acids in the presence of weaker acids.[39]

An apparatus has also been devised for measuring the density and the amount of salts in a liquid by means of its electrical conductivity at a definite temperature. The current is derived from two electrolytic cells connected with an alternating current galvanometer and a recorder. A method of this sort should prove useful for following the progress of concentration of liquids being evaporated.[40]

A method of estimating vanadic acid has been based on its reduction in the presence of sulphuric acid by means of anodes of silver or copper in rapid rotation in an electrolytic cell, or by means of a rotating cylinder of zinc. Over-reduction is prevented by the addition of silver sulphate, and the completion of the reduction is shown by the appearance of metallic silver. The liquid is then filtered and the vanadium estimated by titration with potassium permanganate. The best results are obtained by the use of silver plated with pure copper.[41]

It has been found that hydrofluoric acid is a useful reagent for electrolytic separations. For example, copper can be quantitatively separated from vanadium, tin, or tungsten and electrolytically deposited from an acid fluoride solution. Uranium and titanium behave in the same way as vanadium. The stannic ion does not appear to be present to any notable extent in acid fluoride solutions of stannic tin, but on adding boric acid to the solution, the tin may then be separated either electrolytically or by means of hydrogen sulphide.[42]

By fractional electrolysis of a dilute solution of the sulphates of gallium and iridium, it is possible to separate the gallium in a pure condition, but it is necessary to repeat the electrolysis about fourteen times.[43]

[39] H. S. Harned and C. N. Laird, *J. Amer. Chem. Soc.*, 1918, **40**, 1213 ; *A.*, ii, 412.

[40] E. E. Weibel and A. L. Thuras, *J. Ind. Eng. Chem.*, 1918, **10**, 626 ; *A.*, ii, 368.

[41] F. A. Gooch and W. Scott, *Amer. J. Sci.*, 1918, [iv], **46**, 427 ; *A.*, ii, 373.

[42] N. H. Furman, *J. Amer. Chem. Soc.*, 1918, **40**, 895 ; *A.*, ii, 277.

[43] L. M. Dennis and J. A. Bridgman, *ibid.*, 1531 ; *A.*, ii, 456.

Water Analysis.

The introduction of rapid methods of examining water for the use of armies in the field has been one of the features of recent work in this branch of analysis.[44] For the rapid determination of the hardness of water on the spot, Blacher's method of titration with potassium palmitate is in general the most suitable, and the reagent is prepared for the purpose in the form of standardised pellets.[45]

It has been found that Wartha and Pfeiffer's method[46] of estimating the hardness is rendered more trustworthy, especially in the case of waters rich in magnesium salts, by increasing the amount of sodium carbonate to 14·5 grams, and that of the sodium hydroxide to 8·01 grams. per litre.[47]

A suggestion has been made that the hardness of water might be estimated by measuring the increase in the surface tension after the addition of calcium or magnesium salts to an alkaline soap solution.[48]

For the rapid estimation of magnesium in water, an alkalimetric method has been devised. The water is rendered neutral to methyl-orange and treated with potassium oxalate in slight excess of the amount equivalent to the calcium present, and then with a measured excess of a mixture of standard alkali hydroxide and carbonate solutions. The liquid is then made up to definite volume and filtered, an aliquot part of the filtrate treated with an amount of calcium chloride equivalent to the excess of potassium oxalate used, and the excess of alkali titrated.[49]

In the colorimetric estimation of lead in water, the salts present have a considerable influence on the intensity of the colour reaction. To obviate this, it is necessary to prepare the standard lead solutions for the comparison from the same water which has previously been freed from lead. Comparisons made with standards prepared from distilled water may give results much too low.[50]

A colorimetric method of estimating minute quantities of vanadium in water has been based on the fact that diphenylamine gives a violet coloration with aqueous solutions of vanadium com-

[44] See *Ann. Report*, 1916, 192.

[45] A. S. Behrman. *Philippine J. Sci.*, 1918, 13 [A], 21 ; *A.*, ii, 206.

[46] J. Zink and F. Hollandt, *Zeitsch. angew. Chem.*, 1914, 27, 235 ; *A.*, 1914, ii, 490.

[47] Wagner, *Zeitsch. öffentl. Chem.*, 1917, 23, 375 ; *A.*, ii, 174.

[48] L. Berczeller, *Biochem. Zeitsch.*, 1917, 84, 149 ; *A.*, ii, 132. Compare *Physical Methods.*

[49] M. Monhaupt, *Chem. Zeit.*, 1918, 42, 338 ; *A.*, ii, 335.

[50] R. Meldrum, *Chem. News*, 1918, 47, 49 ; *A.*, ii, 83.

pounds acidified with hydrochloric acid. The test is capable of detecting 0·002 per cent. of vanadium, and is not affected by small quantities of iron, titanates, or nitrates, but in the presence of free nitric acid the method would require modification. For a quantitative estimation, the colour may be compared with that given by solutions containing known quantities of ammonium vanadate.[51]

In Riegler's colorimetric method of estimating phosphoric acid in water, the hydrazine sulphate may conveniently be replaced by stannous chloride.[52]

A new colorimetric method has also been devised for the detection of nitrites in water. The sample is treated first with antipyrine solution, then with mercuric sulphate solution, and finally with a few drops of potassium ferricyanide solution, a red coloration being produced in the presence of a trace of nitrite. The test is also applicable to nitrates after reduction to nitrites.[52]

<div style="text-align:right">C. AINSWORTH MITCHELL.</div>

[51] V. L. Meaurio, *Anal. Soc. Quim. Argentina*, 1917, **5**, 185 ; *A.*, ii, 135.

[52] P. N. van Eck, *Pharm. Weekblad*, 1918, **55**, 1037 ; *A.*, ii, 370.

[53] Escaïch, *J. Pharm. Chim.*, 1918. [vii], **17**, 395 ; *A.*, ii, 273.

PHYSIOLOGICAL CHEMISTRY.

Sir Henry Thompson, late Professor of Physiology at Trinity College, Dublin, whose death was due to the dastardly outrage which sank the *Leinster*, was the only individual who before the war had taken the trouble to estimate a nation's actual food supply—imported and home produced—in terms of protein and calories. The items as found in the returns of, say, the Boards of Trade and Agriculture—so many tons of this and so many tons of that—tell little on mere inspection with regard to the nutritive value of the supply. Thompson, however, had made the necessary calculations in the case of Ireland some time before the war. The interest he took in such matters led to his becoming a member of the Royal Society Food (War) Committee. He went as a representative of that Committee to the Ministry of Food, and afterwards became scientific adviser to the Ministry. The honour of knighthood which was the reward of his official services was enjoyed for a period most sadly brief. Thompson was an enthusiastic student of the science of nutrition, and, although *no trained chemist*, he had other high qualifications as a worker at the subject. His teaching and influence will be greatly missed.

The papers dealing with the dynamic side of physiological chemistry—the processes of metabolism—to which I have hitherto given chief attention in these Reports have been few and, for the most part, unimportant this year. I shall therefore give more attention than usual to other aspects of the subject.

Emulsoid Colloids: Carbon Dioxide in Blood.

It is justifiable to recall sometimes that in this country occurred, not only the birth of colloid chemistry, but its awakening to present activity. Graham presided at its birth and endowed it with much material for growth; but the infant science promptly went to sleep for more than thirty years. Linder and Picton in 1892 began to make important provision for its future, but its

actual awakening to what has since become so robust an existence was due to W. B. Hardy, whose studies were stimulated by the needs of biology. I think that anyone who reviews the literature before and after 1899, when Hardy's first papers were published, will be convinced of the essential rightness of this claim. Afterwards came " German industry " and—the deluge.

After two decades, however, of intensive study of the colloid state, we have hitherto lacked really illuminating knowledge of emulsoid as distinct from suspensoid systems Generalisations from studies of the latter have dominated theory. Yet, theoretically and in practice, emulsoid dispersion is at least of equal importance with suspensoid dispersion. In physiological chemistry it is of particular interest, because the *mise en scène* for the drama of metabolism is largely built of emulsoids.

An enlightened study of an emulsoid colloid by S. P. L. Sörensen and various co-workers, of which the results appear in a monograph recently published, will be greatly welcomed by all who have felt the lack of accurate information concerning the properties of proteins in " native " solution. The monograph can now be obtained in an English translation, which for some reason is called on its title-page "Edition Française." [1] It may be noted that a whole number of the *Zeitschrift für physiologische Chemie* is devoted to a reproduction of the work.[2]

Sörensen has attacked the subject by means of an intensive study of a single substance, regarding it simultaneously from a chemical and a physico-chemical point of view. The material used was crystalline ovalbumin prepared by the method described by F. G. Hopkins and S. N. Pinkus. It was shown long ago that, so far as constancy of optical relation after successive recrystallisations could be a guarantee of purity, the albumin obtained by this method is a pure product.[3] Sörsensen found it to represent material so well defined as to allow of an exact reproduction of conditions in each experiment of a series. The work described in the monograph was done on rigidly quantitative lines. Much of the technique was original. The results are fully discussed and the conclusions are drawn with much insight.

Perhaps the most fundamental part of the work is the proof that the essential phenomena exhibited by emulsoid solutions can be interpreted by the laws which hold for true solutions. The making of sharp distinctions between colloid and crystalloid solution is not justified; the emulsoid is a bridge between the suspensoid

[1] *Comptes rend. Trav. Lab. Carlsberg*, 1907, **12**.
[2] *Zeitsch. physiol. Chem.*, 1918, **103**, 1.
[3] F. G. Hopkins, *J. Physiol.*, 1900. **25**, 206 ; *A.*, 1900, i, 466.

and the crystalloid. In a chapter dealing with the conditions of equilibrium between the crystals of albumin and the constituents of their mother liquor, it is shown that Gibbs's phase rule is perfectly applicable to the system. The osmotic pressure of solutions of the albumin was submitted to an elaborate investigation. Donnan's formula is successfully elaborated to suit the particular conditions present, and it is finally shown that the osmotic pressure of a correctly defined emulsoid solution is as real and as constant a quantity as that of any crystalloid solution of definite composition. Such conclusions as these, and there are others of almost equal importance, are arrived at after a very careful study of a number of individual variables. The monograph is long, extending to 370 pages. It is impossible, therefore, to give even an epitome of the experimental details contained in it, but I may add that, apart from the results, the technique described will afford real help to other workers.

The importance of the purely physical properties of the blood-proteins as emulsoid colloids in maintaining the normal relations of the circulation has been rather overlooked of late. This is owing perhaps to the success with which many isolated organs can carry out their functions when perfused with non-colloidal solutions, such as oxygenated Ringer's or Locke's solution. The needs of medical and surgical practice during the war have once more emphasised the importance of the colloids. When simple saline solutions are used in attempts to restore the blood pressure after it has been lowered by hæmorrhage or shock, no more than a temporary rise is obtained, and the condition may quickly become worse than before treatment. The intravenous injection of a solution containing 6 per cent. of gum acacia and 0·9 per cent. of sodium chloride will, on the other hand, permanently restore the normal blood pressure.[4] Gelatin solutions of the same concentration are also effective, although they are more liable to show some toxicity.[5] The osmotic pressure of the colloids, and perhaps their viscosity, must be supposed to play the chief part in producing this notable effect, and the proteins of normal blood owe much of their importance in the circulating fluid to their colloidal attributes.

It would be a grave mistake, however, to take a view of their functions which is too purely physical. The one function we have to deny to the blood proteins is that of representing nutritive

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[4] W. M. Bayliss, *Med. Res. Committee Reports of the Special Investigation on Surgical Shock and Allied Conditions*, No. 1, November, 1917.

[5] H. Drummond and E. S. Taylor, *ibid.*, No. 3, 1918 ; W. M. Bayliss, *Proc. Roy. Soc.*, 1916, [B], 89 ; W. M. Bayliss, *Proc. physiol. Soc.*, J. *Physiol.*, 1918, 52, XVII.

material in course of transport from gut to tissue.[6] In the chemical equilibrium of the blood itself they undoubtedly play an important part, although the extent of it is just now the subject of fresh discussion. Sörensen[7] insists that at the bottom of the differences between suspensoid colloids and emulsoid colloids lies the fact that the latter, unlike the former, when forming the dispersed or internal phase of a system, react chemically on the external phase. The chemical nature of the particles has relatively small influence in determining the properties of suspensoid solutions. In emulsoid solution, the chemical properties of the dissolved material are of much greater importance. Ostwald's dictum that colloid chemistry is "the science, not of colloid materials, but of the colloidal condition," is untrue when emulsoids are concerned.

In last year's Report I dealt at considerable length with the neutralising power of blood—with its so-called "alkali-reserve." I pointed out that the buffer action of the blood has, since the theoretical and experimental studies of L. J. Henderson, been attributed almost entirely to the inorganic salts present; in the case of the plasma, almost exclusively to the sodium bicarbonate. The claim that the proteins, as amphoteric substances, play an important part in maintaining the hydrion concentration has, however, been again raised,[8] and again sharply criticised.[9] It is sure that the "reactivity" of pure proteins is too small to contribute more than a small proportion of the buffer effect observed when, by the addition of acid or alkali to blood, the hydrion concentration is made to change within the very narrow limits which are physiological. I am not quite sure, however, that all such factors of equilibrium in the blood are yet understood.

Sörensen devotes an important section of his monograph to a mathematical discussion of the capacity of ampholytes in general, and of albumins in particular, to combine with acids or bases, both in salt-free solutions and also, an important addition, in solutions containing neutral salts. I feel unable to make this discussion intelligible here, but it should be read by those who are working at the subject.

If the buffer mechanism of the blood still offers difficulties, so also, and to a greater extent, does the closely related subject of carbon dioxide transport by the blood.

That the bicarbonate of the plasma plays, at any rate, a very important part in stabilising the reaction of the blood is sure.

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[6] For evidence of this on somewhat new lines, see S. Hanson and I. McQuarrie, J. Pharm. Expt. Ther., 1917, 10, 261.

[7] Loc. cit.   [8] B. Moore, Brit. Med. J., 1918, i, 920.

[9] W. M. Bayliss, ibid., 1918, ii, 578.

Does it also represent the combination in which carbon dioxide is carried from the tissues to the lungs? It has been recently shown [10] that bicarbonate does not dissociate at all when exposed to the carbon dioxide tension of the alveolar air. At the temperature of the body, sodium bicarbonate does not dissociate until the carbon dioxide tension is reduced to 2·25 mm. of mercury, whereas the tension in the lungs is of the order of 40 mm., at which a solution of the salt actually absorbs carbon dioxide. It is clear, therefore, that if all the carbon dioxide from the tissues arrives in the lungs as bicarbonate, there must be some mechanism to secure its evolution from the salt.

It has long been taught in explanation of the familiar fact that intact blood gives up the whole of its carbon dioxide to a vacuum that the proteins play a part as weak acids, and it has been implied, perhaps more vaguely, that they play a similar part when the bicarbonate of the blood is exposed to the carbon dioxide tension of the lungs. Evidence has recently been brought forward,[11] however, which throws doubt on their capacity to act in this way either in the former case or the latter.

The special case of hæmoglobin must, however, be considered, and from two points of view. I mentioned in my last Report the statement that hæmoglobin has special properties as an ampholyte, acting as a buffer to a degree of which the plasma proteins are incapable, and also becoming more acidic on passing from the reduced to the oxygenated condition.[12] Hæmoglobin itself also enters into combination with carbon dioxide, the compound becoming less stable with increasing tension of oxygen.[13] Oxygenation in the lungs therefore drives out carbon dioxide from its combination with blood pigment, and also, independently, causes an increase of hydrion concentration within the corpuscles. The corpuscles are, however, permeable to anions, and changes of equilibrium begun in the corpuscles extend to the plasma. In these facts we have a basis for explaining, at least in part, the removal of carbon dioxide from bicarbonate in the lungs. The direction of these changes must be reversed in the tissues where carbon dioxide tension is much higher and the oxygen tension nil. The information available, however, although becoming much more quantitative than before, is not yet quantitative enough for measuring the relative importance of this or that factor, nor to give a complete picture of carbon dioxide transport.

[10] G. A. Buckmaster, *Proc. physiol. Soc., J. Physiol.*, 1918, **52**, xvi.

[11] G. A. Buckmaster, *J. Physiol.*, 1917, **51**, 105.

[12] *Ann. Report*, 1917, 178.

[13] J. Christiansen, C. G. Douglas, and J. S. Haldane, *ibid.*, 1914, **48**, 244 ; *A.*, 1914, i, 1012.

It is surprising, perhaps, that in so fundamental a matter physiological knowledge should be yet to seek. As a matter of fact, however, as I claimed in a recent Report, the advances of recent years towards an understanding of equilibrium in the blood have been remarkable, and progress continues. Yet the teaching, as I remember it, of twenty-five years ago was not wrong. As a sketch it was correct. We are now filling in the details of the picture, and the details are difficult.

It is necessary that we should know more of the properties of emulsoid colloids. Just as the gain in the purely chemical knowledge of the composition of the proteins has helped to illuminate metabolism, so, I think, will more knowledge of the physical-chemical properties of native proteins in solution throw light on such phenomena as those just discussed. Hence the importance of Sörensen's new work on the emulsoid colloids, which possess so much more reactivity than the better understood suspensoids.

Some Other Relations of the Blood Proteins.

A few other points concerning the blood proteins may now be mentioned. It is likely that, as Hardy's pioneer work suggested, the condition of the euglobulins (not the pseudo-globulins) differs from that of the albumins in coming nearer to suspensoid than to emulsoid dispersion. It seems to partake of the qualities of both, and the globulin system illustrates the point insisted on by Graham, and recently by Sörensen, that many gradations can be found between a mere suspension of particles and true crystalloid solution. Since we now know that the globulins really differ chemically from the albumins, their relative fluctuations in the blood become of no small interest. The ratio has been redetermined recently, and it seems to be constant in the same individual while in normal health, but differs widely in different individuals, the albumin fraction varying from 55 to 85 per cent. of the whole proteins, and the globulins, including, of course, the pseudo-globulins, from 45 to 70 per cent. Injecting foreign proteins has no permanent effect on this ratio, which is rapidly readjusted.[14] There is, however, a large relative increase in the total globulins during injections of diphtheria or tetanus antitoxins.[15] Fibrinogen as a special globulin is greatly increased by a first injection of peptone, but markedly depressed (negative phase) by a second injection at the right interval. The injection of vaccines, tuber-

[14] Esther Smith and C. L. A. Smith, *J. Immun.*, 1917, **2**, 343.
[15] K. F. Meyer, S. H. Hurwitz, and L. Taussig, *J. infec. Dis.*, 1918, **22**, 1.

culm, etc., increases fibrinogen.[16]   Older observations had suggested some of these recent findings.   Whether these factors increase the globulin fraction by causing transference of protein from the tissue to the blood, or in some other way, the increase is an interesting point.   The suggestion made some time ago that the euglobulins represent protein–phosphatide complexes seems to be confirmed in various papers since published.   This should be remembered in connexion with the discussion of phosphorus complexes in a later section.   The distribution of phosphorus, organic and inorganic, in the blood is now being carefully studied.[17]

Chemical Factors in Shock.

I have referred to the successful use of gum arabic solutions in the treatment of circulatory failure due to shock.   An understanding of the factors concerned in producing ` shock " has been one of the great needs of war-time, and much excellent contemporary research has been done under the stimulus of that need.   Metabolic chemical factors are suspected of playing a part in producing shock, and although this aspect of the subject has proved elusive, the studies made deserve reference.   Some of the facts elicited are related to those dealt with at the end of the last section, and extend somewhat the ground covered by the discussion on the alkali reserve of the blood in last year's Report.

Rather more than a year ago, observations made on wounded soldiers in France were thought to suggest that acidosis," defined as a serious reduction in the alkaline reserve of the blood, is a causative factor in the production of shock.[18]   It was believed for a time that lactic acid, produced in the injured moribund muscles, was the cause of this acidosis, so that a very simple chemical factor seemed to relate the receipt of a severe wound with the subsequent condition of shock.   This conception, however, did not survive a discriminating experimental study of the matter.[19]   When certain disturbing factors had become understood and were eliminated, it could be shown that a reduction of the alkali reserve of the blood, even if severe and long maintained, does not cause shock.   Nor does it, indeed, cause any perceptible impairment of the circulation or any observable symptoms of importance.   This conclusion

[16] G. Modrakowski and V. Orator, *Wien. Med. Woch.*, 1917, **30**, 1073.

[17] J. Feigl, *Biochem. Zeitsch.*, 1917, **83**, 81 ; **84**, 231 ; **87**, 237 ; *A.*, i, 50, 203, 357.

[18] A. Wright and Fleming, *Lancet*, 1918, i, 205.

[19] *Med. Res. Committee, Reports of the Special Investigation Committee on Surgical Shock and Allied Conditions*, No. 7, Acidosis and Shock.

is one which might well have been expected, because it was already
known that the alkali reserve might be greatly reduced without
any increase in the hydrion concentration of the blood, and it is
only on changes in the latter that, theoretically at least, we should
expect symptoms to supervene.   The laborious experiments under-
taken to establish the point would perhaps never have been done
save for certain mistakes in the interpretation of the earlier ex-
periments.   That these mistakes were made is no matter for regret,
for the work done in consequence has yielded some quite interest-
ing results and has shown, incidentally, that the Van Slyke
technique for the estimation of alkali reserve is a trustworthy and
convenient aid to clinical observation.

It has been thoroughly established by the experimental work
referred to that a grave depletion of the alkali reserve is indeed
invariably associated with such conditions as shock, but as a
secondary result and not as a primary factor.   It follows on
deficiency in the oxygen supply to the tissues, which itself results
from the failure in the circulation.   With lack of oxygen, the
accumulation of (lactic) acid in metabolism inevitably involves
such a result.   This, again, is by no means an unexpected revela-
tion, but it is satisfactory to have such complete experimental
demonstration of this objective change in the body occurring as a
result of deficiency of oxygen.   As I endeavoured to emphasise in
the last Report, observations show that although an individual in
whom the alkali reserve is diminished may display no symptoms,
because the actual chemical reaction of his blood may be unaffected,
he is yet in a different position from one who has a normal alkali
reserve.   The former may become perceptibly dyspnœic on slight
exertion, and more intensely dyspnœic with an equally great exer-
tion than the latter.   This fact has been very fully demonstrated
in these recent studies.   The effects of want of oxygen have, in
fact, dominated what may be termed war physiology.   The study
of these effects became necessary in connexion, not alone with shock,
but with the results of gassing and the reaction of individuals to
high altitude flying.   Many interesting details have been added to
our knowledge of the results of oxygen deficiency as a result of
these war studies.

The investigations into shock have yielded results of general
interest, some of which may be mentioned.   The parallelism which
obtains between degrees of reduction in the blood-pressure and
the consequent fall in available blood-alkali is striking enough, no
matter how the former may have been brought about.   There is
a critical pressure above which no effect on the alkali reserve is to
be observed.   This, in the case of human beings, as well as of dogs

and cats, lies in the neighbourhood of 90—80 mm. of mercury. Thus, taking a mean of a number of clinical cases, at a blood pressure of 90—100 mm. the carbon dioxide capacity (which measures the alkali reserve) of the plasma was 49 vols. per cent. At 60—70 mm. it was 36 vols., and at 50—60 mm. only 24 vols. per cent.

Not only does the mere existence of acidosis fail in itself to produce shock, it has no effect in favouring the production of shock by other agencies. It does not exaggerate, for instance, the effects of hæmorrhage. The functions of the vaso-motor centre in maintaining the normal blood pressure remain normal in conditions of acidosis. Acidosis does not modify the action of adrenaline nor the "shock" effect of peptone or histamine.[20]

Mention of the last substance introduces what remain the most interesting possibilities relating to the play of chemical factors in shock. It is well known that histamine (β-iminazolylethylamine) in large doses produces symptoms astonishingly like those of anaphylactic shock, and the latter has many features in common with surgical shock. A paper dealing with a detailed study of the vaso-dilator effects of histamine has appeared during the year.[21] The action of the base would seem to be on the capillaries rather than on the arteries or arterioles, and the fall of pressure in surgical shock is almost certainly due to a similar capillary dilatation. The probability that metabolites with an action like that of histamine are normally formed during the activity of the tissues is very great, and forms the readiest explanation of the capillary dilatation which accompanies increased activity.[22] There is something more than a possibility that such substances appear in greater amount in damaged tissues, and the universal capillary relaxation which is a central feature of shock, although certainly not an effect of acid production, may yet be due to the absorption of histamine-like substances produced in extensive wounds.

Biochemistry of Guanidine Compounds.

I devoted a short section in my last Report to the action of guanidine in producing the symptoms of tetany. The subject is of great interest and importance, and has progressed somewhat during the year. That guanidine as a drug stimulates muscles has been long known.[23] That in strong doses it produces, on the

[20] *Med. Res. Committee Report, loc. cit.*

[21] H. H. Dale and H. N. Richards, *J. Physiol.*, 1918, **52**, 110.

[22] Compare J. Barcroft and H. Piper, *ibid.*, 1912, **44**, 359 ; *A.*, 1912. ii, 782.

[23] Gergens and Baumann, *Pfluger's Archiv*, 1876, **12**, 205.

other hand, a curare-like action in frogs, and that, being strongly dissociated in solution, its action is that of a powerful base acting in the form of an organic cation, has been known since 1907; so also has the fact that its physiological action is counteracted by calcium salts.[24]   A little later it was shown to produce two effects in muscle, one displayed in spontaneous twitching, the other in a modified response to nerve stimulation.   It was suggested that it acted on two different substances in the muscle.[25]   Meanwhile, the base, methylguanidine, had been shown to be present in small amounts as a normal constituent of muscle,[26] and also found in normal urine.[27]

In 1912—1913, the methylated base was shown to be present in much more than the normal amount in the urine of dogs which had undergone parathyroidectomy.   If after this operation methylguanidine showed less increase, other guanidine bases, guanidine itself, for instance, and dimethylguanidine, were said to take its place.   In connexion with the statements made in the last section, it is of interest to note that histamine was also identified in the urine of dogs which had undergone the operation, although only in three cases out of six.   In a discussion of the above findings, the suggestion was made that the guanidine bases are responsible for the symptoms displayed after loss of the para- thyroids, but not with definite reference to tetany.[28]

Then (1917) followed the clear experimental proof referred to in the last Report that guanidine bases were greatly increased in the blood and urine both of clinical cases of tetany and of para- thyroidectomised dogs, together with the demonstration that the effect of administering guanidine is to produce symptoms identical with those seen after removal of the parathyroids.[29]   This year, the identity of effect has been still further established by the proof that the hypoglycæmia which is characteristic of a loss of the para- thyroid function is also produced by the administration of guanidine salts, and, no less, the equally characteristic acidosis and increased excretion of ammonia.   There would seem to be one point of difference, however—in the case of the rabbit, at any rate

[24] H. Fühner, *Zentr. Physiol.*, 1907, **20**, 838 ; *A.*, 1907, ii, 901.

[25] M. Camis, *J. Physiol.*, 1909, **39**, 73 ; *A.*, 1909, ii, 819.   See, for more recent work on this point, J. S. Meighan, *ibid.*, 1917, **51**, 51.

[26] R. Krimberg, *Zeitsch. physiol. Chem.*, 1906, **48**, 412 ; *A.*, 1906, ii, 781.

[27] F. Kutscher and A. Lohmann, *ibid.*, 1, 422 ; **49**, 81 ; *A.*, 1906, ii, 471, 786, 875.

[28] F. W. Koch, *J. Biol. Chem.*, 1912, **6**, 451 ; 1913, **15**, 43 ; *A.*, 1912, ii, 1194 ; 1913, i, 735.

[29] *Quart. J. exp. Physiol.*, 1917, **10**, 175 ; *Ann. Report*, 1917, 195.

—in that, unlike the tetany induced by removal of the glands, that which follows guanidine administration is not abolished by giving calcium salts.[30] Such a contrast may depend, however, on no more than the inevitable difference of conditions involved in the direct administration of the base on the one hand and its gradual production in the body on the other. Another phenomenon which is seen in the absence of the glandular function, and results also from guanidine injection, the arrest, namely, of the vago-cardiac inhibition, has been shown to be removed in each case by giving calcium salts.[31]

The proof that the action of guanidine is responsible for so familiar a pathological condition as tetany, and the possibility that the pathological action is simply an exaggeration of a physiological function, certainly make the whole question of guanidine metabolism a very interesting one. We want to know how to relate together, in terms of metabolic change, arginine, with its guanidine nucleus, the guanidine bases themselves, and creatine with its methylated guanidine grouping. The extraordinarily elusive functions, or meaning in metabolism, of the last-mentioned substance now gain renewed interest.

It seems likely enough that both guanidine and creatine arise from arginine, although I do not feel that the point is actually proven in either case. It was to be expected, perhaps, that guanidine takes its direct origin from creatinine, but as after parathyroidectomy the free guanidine of the muscles decreases and the creatine increases more or less proportionately,[32] there is some suggestion for the reverse relation. Maybe there is only a shift of the equilibrium which exists between them.

Does creatine arise from arginine? An endeavour to answer this question formed the last as well as some of the earliest scientific work of W. H. Thompson,[33] to whose tragic death I earlier referred. He administered arginine carbonate, by the mouth or by injections, to ducks, dogs, and rabbits. On a diet free from pre-formed creatine, the only safe condition for experiment, administration by the mouth of 2 grams of the arginine salt to dogs gave an average extra excretion of 23·6 milligrams of creatine, estimated as creatinine (pre-formed creatinine was not usually affected), in the urine, corresponding with an increase of 10 per cent. in the daily output of creatinine, and representing about 2·5 per cent. of the guanidine nucleus of the arginine given.

[30] C. K. Watanabe, *J. Biol. Chem.*, 1918, **33**, 253 ; **34**, 51, 65, 73 ; *A.*, i, 205, 327.   [31] D. Burns and A. M. Watson, *J. Physiol.*, 1918, **52**, 88.
[32] P. S. Henderson, *ibid.*, 1 ; *A.*, i, 279.
[33] W. H. Thompson, *ibid.*, 1917, **51**, 111, 347 ; *A.*, 1917, i, 673 : 1918, i, 88.

Approximately the same results were given in the case of birds. Somewhat larger increases, amounting in dogs to 22 per cent. of the normal excretion of creatinine, were found after hypodermic or intravenous injection. It is remarkable that a second administration did not show the effect. It is remarkable, too, that a larger percentage of the guanidine nucleus seemed to appear as creatine when racemised arginine was given.

Estimations of creatine in the muscles of rabbits were made before and after injections of from 1·5 to 3·1 grams of arginine carbonate, the muscles of the one limb being removed before the injection, and those of the corresponding limb on the opposite side six hours after it. Possible changes in water content during the experiment were controlled.

The results were all consistent (seven observations) in showing a higher percentage after arginine injection, but the increase was very small. In one experiment, it is true, the creatine was increased by 8 per cent., but in two by only 2 per cent., and on the average by only 3 per cent. In later experiments, the arginine was given in company with substances which were presumed able to supply a methyl group for the methylation of the guanidine nucleus, for instance, methyl citrate and methyl benzoate. The former of these seemed definitely to increase (on injection, not after feeding) the amount of creatine formed from a given amount of arginine, whilst the latter had no such effect. With methyl citrate, after correction was made for the rather noteworthy circumstance that this substance when administered alone gave some increase, the plus excretion was found to account for 7 per cent. of the guanidine nucleus in the arginine injected. Experiments in which the arginine was combined with betaine or choline did not show that this type of methylated compound increased the power of the arginine to affect the urinary creatine or creatinine.

Much larger increases were seen when, with the arginine, paraformaldehyde or hexamethylenetetramine was injected into ducks, but an increase nearly as large followed the administration of the formaldehyde alone, so there was no proof that the arginine administered at the time was converted into creatine. If formaldehyde, in whatever way, really increases the production of creatine on synthetic lines, it is a noteworthy fact. We have to think, however, of the possibility that a toxic breakdown of muscle substance may be responsible for the increase. Thompson himself suggests that the reactions involved are those which form the basis of Werner's theory of the methylation of amino-compounds by formaldehyde.[34]

³⁴ W. H. Thompson, *Biochem. J.*, 1917, **11**, 307 ; *A.*, i, 142.

The injection of guanidine carbonate increased the total urinary creatinine to a degree which would indicate methylation of some 10 per cent. of the base administered. It does not seem certain, however, that Folin's method, which was used for the estimations, might not return as creatinine some other derivative of the injected guanidine.

It seems to me that this very laborious and praiseworthy experimental study (of which the accounts abound in detail), whilst most certainly adding strength to the probability that creatine arises from arginine, cannot be said altogether to prove that it does so.

Other recent observations [35] have been made on somewhat similar lines, although involving very few experiments. In one experiment, the injection of 2 grams of arginine increased the urinary creatine (expressed as creatinine) of a dog from 6·4 to 16 milligrams without affecting the pre-formed creatinine. The authors attach no importance to this result, because an injection of histidine carried out as a control produced a similar effect. In so arguing, they neglect the fact that arginine and histidine have been shown to be largely capable of replacing one another in metabolism.[36] However, in a second experiment with arginine the effect was not obtained.

I have ventured elsewhere [37] to point out that experiments of the kind just noticed do not necessarily give favourable conditions for proving whether a given reaction in metabolism starts initially from this or that substance. Knowing, for instance, as we do, that the creatinine of the urine is practically unaffected by the widest variations in the protein intake, and is therefore independent of the amount of arginine absorbed during digestion, we should scarcely expect it to be affected by an increase in the supply of arginine given in free form. Creatine itself might be formed and yet not be excreted. Nor is it likely that the latter would in any case be appreciably increased in the muscles under such conditions as those described. When an animal is in a state of adequate nutrition, it does not follow that a particular process in its tissues will be appreciably affected by a mere increase, and especially a very temporary increase, in the supply of the precursor from which the process normally starts. Otherwise, there could not be that distinction between endogenous and exogenous metabolism which is usually recognised. Of the relative stability of the former, creatinine is the most conspicuous example. The tissue cell as a

[35] L. Baumann and H. M. Hines, *J. Biol. Chem.*, 1918, **35**, 95 ; *A.*, i, 417.

[36] H. Ackroyd and F. G. Hopkins, *Biochem. J.*, 1916, **10**, 551 ; *A.*, 1917, i, 237.

[37] H. Ackroyd and F. G. Hopkins, *loc. cit.*

chemical system does not, of course, escape from the laws of chemistry: an increase *in loco* of the concentration of specific material must accelerate the reactions which that material normally undergoes. In some cases, such, for instance, as that of urea formation from amino-acids, we find an immediate effect from an increase in the concentration of the precursors. This, indeed, is the real characteristic of what we call exogenous metabolism. In the case of reactions which are part of the basal and essential, as distinct from the more accidental (often self-protective), activities of a tissue, the velocity is much more independent of the supply of raw material, because, owing to the organisation of the cell, any excess does not arrive at the locus of that particular change. The excess is got rid of by other less specific reactions, hydrolysis and direct oxidation, for example (exogenous change), and has but a temporary existence in the cell. That some regulating mechanism can, as it were, be forced by a large increase of concentration round the cell, may possibly account for small changes such as the increase of creatine in the above experiments.

Other papers dealing with creatine and creatinine from aspects different from the above have appeared during the year. Only one, I think, calls for notice. To test once more the question of a supposed relation between creatine and carbohydrate metabolism, advantage was taken of the fact that in ruminants creatine is normally excreted as well as creatinine. In these animals, it was found that the excretion of the former is in inverse proportion to the amount of carbohydrate in the diet. It is plausibly argued from the evidence given that creatine is produced in metabolism in relatively large quantities, that it is utilised in the tissues, and that its utilisation is intimately connected with the metabolism of carbohydrate. So far as the conversion of creatine into creatinine is concerned, it is suggested that when the former is produced within the metabolic field, it is probably in a more favourable position for such conversion (if this takes place) than is creatine given by the mouth or by injection. The amount converted depends on some metabolic process which is not affected by the amount offered for conversion.[38] This point of view is, clearly, the one which I have myself urged—in more detail and with less caution—in the preceding paragraphs.

[38] B. Orr, *Biochem. J.*, 1918, **12**, 221 ; *A.*, i, 561.

The Phosphoric Acid Complexes of Living Cells.

Since, in 1911, Professor Halliburton[39] gave an account of research done on nucleic acids, these important substances have received no attention in these Reports. The work of the Rockefeller Institute towards the end of the last decade extended the results of the earlier studies and left our knowledge of thymusnucleic acid in a satisfactory state, although there is still uncertainty about the details of its molecular structure.[40] Of late, attention has been given rather to yeast-nucleic acid. No evidence has yet appeared to shake the general belief that the nucleic acids of all animal cells are identical with the former substance,[41] and those of all vegetable cells with the latter. The two nucleic acids are therefore exceedingly widespread in nature and of great biochemical importance.

In an interesting address, P. A. Levene[42] has remarked that such apparent lack of differentiation in the nuclear material of living tissues was scarcely to be expected. It removes part of the evidence for the view that underlying the morphology of species is a chemistry of species. There are, however, countless other opportunities in the cell for chemical variation. The uniformity of the nucleic acids would seem to point to the fact that their structure is something fundamental to the make-up of the cell—something essential to the life of all tissues.

It will be recalled that the essential chemical structure of the nucleic acids is that of polynucleotides. In the simplest type of nucleotide—the mononucleotide—orthophosphoric acid is condensed with a carbohydrate and a purine or pyrimidine base, the carbohydrate residue being intermediary, linking the acid to the base. Such are guanylic acid (phosphoric acid-*d*-ribose-guanine), first isolated from the pancreas, and inosic acid (phosphoric acid-*d*-ribose-hypoxanthine) from muscle. These mononucleotides, however, are not found as such in the nuclei of the cells, but are to be looked on rather as metabolites of the true nucleic acids, and, so

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[39] *Ann. Report*, 1911, 199.

[40] For literature up to 1913, see " Nucleic Acids : their Chemical Properties and Physiological Conduct," by Walter Jones. Longmans, 1914. Monographs of Biochemistry.

[41] See, however, R. Nakasako, " Nucleic Acid of the Lymph Corpuscle." *A. C. James Research Lab.*, 1917, Bull. 3, 29 (*Physiol. Abstr.* 1918, **3**, 4). I have not seen the original of this paper. The author claims to have isolated xanthine and hypoxanthine as well as guanidine and adenine. All previous experience would suggest that enzymic deamination had occurred before or during the preparation of the material.

[42] *J. Amer. Chem. Soc.*, 1917, **39**, 828 ; *A.*, 1917, ı, 363.

far as the two just mentioned are concerned, as being probably derived from vegetable food consumed by the animal.

Six years ago it was well established that in thymus-nucleic acid four different mononucleotides, containing respectively the bases adenine, guanine, cytosine, and thymine, are linked together. Less certain is the exact grouping of these four constituents of the molecule and the nature of the linkings, although the structural formula suggested by P. A. Levene has met with general if only provisional acceptance.[43]

For a considerable time there has been the suggestion that yeast-nucleic acid is also composed of four mononucleotides linked together, the difference between the vegetable and the animal product being that in the former the carbohydrate of each group is *d*-ribose instead of a hexose (see below), whilst a uracil-mononucleotide replaces the thymine-mononucleotide.

Recent work has provided confirmatory evidence for the existence and nature of the four mononucleotides, and nothing has arisen to suggest that the molecule of yeast-nucleic acid contains any other essential element in its structure. From the products of its partial hydrolysis, guanylic acid,[44] as well as uridine-phosphoric acid (uracil mononucleotide), and cytidine-phosphoric acid (cytosine mononucleotide), have been prepared pure, whilst the fourth nucleotide, containing the adenine group, has·also been separated with a reasonable guarantee of purity.[45]

In the case of the vegetable nucleic acid, however, there is, even now, less evidence for the actual grouping of the mononucleotide constituents and for the position of the linkings than can be claimed in the case of the animal product. The effort to get the evidence has naturally been made on the lines of studying the products of carefully limited hydrolysis. It was the isolation of such products—dinucleotides, for example—which threw light on the structure of thymus-nucleic acid.

It has been recently stated that yeast-nucleic acid, either by enzyme hydrolysis[46] or, more simply, by heating with ammonia,[47] could be made to yield two intact dinucleotides, the one containing adenine and uracil, the other guanine and cytosine. It was further claimed that from the products of controlled hydrolysis by acids a third dinucleotide containing cytosine and uracil could be

[43] P. A. Levene and W. A. Jacobs, *J. Biol. Chem.*, 1912, **12**, 411 ; *A.*, 1912, i, 926.

[44] B. E. Read, *ibid.*, 1917, **31**, 47 ; *A.*, 1917, i, 596.

[45] P. A. Levene, *ibid.*, 1918, **33**, 229, 425 ; *A.*, i, 130, 240.

[46] W. Jones and A. E. Richards, *ibid.*, 1915, **20**, 25 ; *A.*, 1915, i, 91.

[47] W. Jones and B. E. Read, *ibid.*, 1917, **29**, 111 ; *A.*, 1917, i, 232.

separated.[48] This evidence, if established, would clearly indicate that the two pyrimidine mononucleotides are linked together and take the central place in the original molecule, whilst the constituents containing purines would be external, the adenine mononucleotide being attached to the uracil mononucleotide and the guanine mononucleotide to the cytosine mononucleotide. Moreover, because the supposed dinucleotides appeared to yield brucine salts containing four molecules of the alkaloid, the suggestion arose that the phosphoric acid hydroxyl groups could not be, as was formerly supposed, concerned in the linking of one mononucleotide to another. The linkings would then most probably involve the carbohydrate groups, and a tetraribose of the structure

$$(C_5H_{10}O_5)_4 - 3H_2O$$
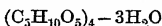
would form, as it were, the essential nucleus of the nucleic acid molecule, which would be in effect a substituted polysaccharide rather than, as in the earlier view, a substituted phosphoric acid.

Unfortunately, this evidence seems to have broken down. The products supposed to be dinucleotides, although they gave consistent analytical figures and crystalline brucine salts, of which the composition remained constant during repeated recrystallisation from methyl alcohol, and also barium salts to correspond, were nevertheless apparently mixtures. By the choice of a special solvent—dilute (35 per cent.) ethyl alcohol—the brucine salts could be in each case separated into two fractions. From each of these was obtained a mononucleotide containing one of the two bases supposed to be in the corresponding dinucleotide.[49]

So far I have been dealing with American work. It has been claimed elsewhere that with controlled hydrolysis by enzymes or weak ammonia, the uracil mononucleotide may be split off, leaving intact a trinucleotide containing the three remaining bases.[50] This claim was first based on the preparation and analyses of a hexa-brucine salt of the supposed trinucleotide, evidence which was rightly criticised as unsatisfactory and insufficient. The trinucleotide, however, has now been further studied[51] and made to yield a dinucleotide containing guanine and adenine. This, as well as the cytosine mononucleotide simultaneously split off, was obtained in a crystalline form. There would therefore seem to be now good evidence for the existence of the trinucleotide from yeast-nucleic

[48] W. Jones and B. E. Read, *J. Biol. Chem.*, 1917, **31**, 39 ; *A.*, 1917, i, 596.

[49] P. A. Levene, *ibid.*, 1917, **31**, 591 ; *A.*, 1917, i, 670. Levene, *loc. cit. supra.*

[50] S. J. Thannhauser and G. Dorfmüller, *Zeitsch. physiol. Chem.*, 1917, **100**, 121 ; *A.*, i, 49.

[51] S. J. Thannhauser and G. Dorfmüller, *Ber.*, 1918, **51**, 467 ; *A.*, i, 316.

acid, and for the particular grouping which its composition indicates. The two purine nucleotides would appear to be adjacent in the original nucleic acid molecule.

In the trinucleotide, six hydroxyl groups belonging to the phosphoric acid radicles are free, so that the linkings probably involve the carbohydrate groups. It would seem, moreover, that the three constituents of the trinucleotide must have a linking different from that which holds the uracil nucleotide in the molecule, since the latter is more easily eliminated by hydrolysis. The suggestion is therefore put forward that whilst in the original nucleic acid all four nucleotides are joined through the phosphoric acid groups, the three present in the trinucleotide have additional linking through the carbohydrate groups. Hydrolysis with dilute ammonia severs only the linking between the phosphoric acid groups.

A brief reference may be made to thymus-nucleic acid. As is well known, the existence of the hexose grouping in this has been accepted on indirect evidence. The sugar has not been isolated, but its nature has been inferred from the yield of lævulose and formic acid on hydrolysis. It is now stated [52] that the "carbohydrate" is really related to glucal ($C_6H_{10}O_4$), a reduction product of glucose first described by Emil Fischer in 1913. It is to be hoped that so important a statement will be duly tested by those who are now working at the chemistry of nucleic acids.

It is clear that recent work on the constitution of these cell constituents has brought us no evidence of a final sort, but I have felt justified in dealing with it at some length because the papers quoted illustrate a gradually developing technique for dealing with what are difficult but, biologically, very important chemical products.

The nucleotide structure, of which there is no doubt whatever, is essentially remarkable. One feels how unlikely it is that pure chemical suggestion would by itself have led to the idea of the existence of natural compounds in which a carbohydrate links phosphoric acid to a base. Yet it is now certain that such compounds play a prominent part in the chemistry of living tissues. Their synthesis should tempt the chemist.

One may remark that yeast-nucleic acid, being extensively employed in medical and surgical practice, is now prepared in this country on a commercial scale. [53] If the product prove to be fairly pure and free from the products of its own partial hydrolysis,

[52] R. Feulgen, *Zeitsch. physiol. Chem.*, 1917, **100**, 241 ; 1918, **101**, 296 ; *A.*, i, 85, 413.

[53] Compare A. C. Chapman, *Analyst*, 1918, **43**, 259.

material for further research has become easy to obtain. Apart
from this, we now possess a relatively easy method for preparing
it in the laboratory.[54]

Brief reference may now be made to allied tissue constituents,
the phosphatides. Because of the difference in their geography
in the cell, and maybe because of the differences in their probable
functions, but chiefly, I think, because of the accident of widely
different solubilities, nucleic acids and phosphatides are usually
thought of apart. From the point of view of intermediary meta-
bolism, however, it is a mistake to forget the circumstance that
whilst the former consist of phosphoric acid in association with a
base and carbohydrate, the latter contain phosphoric acid associated
with a base and a fat. The resemblances and the differences
in the chemical make-up of these substances are alike sugges-
tive.

A summary of the difficult and scattered literature of the phos-
phatides has appeared during the year in a monograph by
H. Maclean.[55] The book, as the author points out in his preface,
was written in circumstances made difficult by the war. It is,
nevertheless, most valuable as an up-to-date account of present
knowledge concerning the phosphatides and lipins. It also contains
just criticism of much literature which does not represent know-
ledge. The author emphasises once more, what even German
writers have of late allowed, that although our knowledge of the
lipins has been materially increased within the last few years, we
really know little to-day beyond what was known and published
by Thudicum more than twenty years ago. "Indeed, recent
advances are in many cases but corroborations of Thudicum's
wonderful experimental work."

I propose to refer only to some advances in connexion with the
purification and characterisation of the chief exemplar of the phos-
phatide group—lecithin itself. Until certain observations by
MacLean[56] were published, most preparations of lecithin accepted
as pure were probably really mixtures in which true lecithin, of
which the basic constituent is choline, was associated with the
related substance kephalin, which contains aminoethyl alcohol as
a base. It was shown that a separation was possible by treating
the mixed cadmium chloride compounds with ether. The absence
of kephalin from a preparation can be demonstrated with ease,
because, unlike choline, its base contains an amino-group, and

[54] G. Clarke and S. B. Schryver, *Biochem. J.*, 1917, **11**, 319 ; *A.*, i, 130.

[55] "Lecithin and Allied Substances ; the Lipins." Monographs on Bio-
chemistry, 1918 : Longmans.

[56] H. MacLean, *Biochem. J.*, 1915, **9**, 357 ; *A.*, 1915, i, 936.

therefore yields nitrogen in Van Slyke's apparatus. Further work in this connexion has been published during the year.[57]

If the cadmium compound of " lecithin " from egg-yolk is re-crystallised from a mixture of ethyl acetate and 80 per cent. alcohol, the true lecithin can be freed from kephalin and then liberated from its cadmium compound by means of ammonium carbonate. Such a preparation seems to be really pure. If, at any rate, it is reduced by hydrogen in the presence of palladium, so as to give the corresponding hydrolecithin, in which both of the fatty acid radicles are saturated, elementary analyses then agree very exactly with theory. Reduced kephalin—hydrokephalin—in which the two fatty acid residues are present as stearyl, has also been prepared so as to give theoretical figures on analysis.

It will be noticed that this satisfactory guarantee of individuality is attached to preparations which have been, so to speak, stabilised by the reduction of unsaturated fatty acid radicles contained in the phosphatide.

Quite apart from the instability displayed during the course of their extraction, the difficulty of preparing individualised sub-stances of this type is, in my opinion, only to be fully understood by recognising that part at least of the metabolism of normal fat, and probably some of the metabolism of carbohydrate, proceed within these phosphorus complexes.

The condition of things in living stuff is never statical—there is rather, so to speak, dynamic equilibrium. Reactions run in successive stages : at first, maybe, in synthetic directions, but ultimately towards end-products which are excreted. These reac-tions are constantly maintained by a supply of new material from the food.

From such a milieu, a chemical individual can be isolated with ease only if, in the series of changes, it happens to be a phase which tends to accumulate.[58] Intermediate products which accumulate in relatively large amounts are those which are responsible for the physico-chemical properties of the cell—those which we look on as part of its structure. Among such, doubtless, are certain of the phosphatides ; but so long as the tissue is alive, the fatty acid radicles in the phosphatides almost certainly undergo desaturation and probably oxidation, whilst the molecule is at the same time continuously reconstructed from a fresh supply of fatty

[57] P. A. Levene and C. J. West, *J. Biol. Chem.*, 1918, **33**, 111 ; **34**, 175 ; **35**, 285 ; *A.*, i, 98, 288, 421.
[58] See on this point F. G. Hopkins, "The Dynamic Side of Biochemistry." Address in Biochemistry, *Rep. Brit. Assoc.*, 1913, 652. *Nature*, **92**, 213 ; also W. M. Bayliss, " Principles of General Physiology," 1st ed., p. 20.

acids. When a main product is isolated, it is therefore likely to be associated with small amounts of related products, and it is not surprising that purification is difficult.

The suggestion that fats may be metabolised when in phosphatide combinations is by no means new, but recent work[59] has given evidence for it on fresh lines. There seems, for instance, to be no doubt that when ordinary fatty acids are being absorbed from the gut after a meal rich in fat, there is a marked increase of phosphatides in the blood, and especially in the corpuscles of the blood. The corpuscles take up at least a proportion of the fat absorbed and build it up straightway into phosphatide complexes. In these, the fatty acids certainly undergo desaturation. A further indication of the instability of the phosphatides in metabolism is found in the presence of a specific lipoidase in leucocytes and pus cells.[60] This enzyme hydrolyses lecithin in feebly alkaline solution. It is more thermolabile than the ordinary lipase associated with it.

It may be noted, in parenthesis, that another synthetic process occurs when fats are being absorbed, for although the total cholesterol in the blood is unaffected by the taking of a fat diet, the amount present in the form of its fatty acid esters is markedly increased during absorption. The cholesterol thus concerned in fat transport seems to be of the ordinary kind, crystallising in rhombic form, whereas in organs such as the kidney a different variety predominates, which crystallises in elliptical form.[61]

What may be the significance of the co-existence of two methods for fat transport—in phosphatide combination and in cholesterol esters respectively—is uncertain. It is clear, however, that the facts just reviewed, together with the circumstance that a great part of true "tissue" fat, as distinct from fat merely deposited, consists of phosphatides, give a very strong suggestion for the metabolic importance of the latter.

Turning now in this same connexion to the fate of carbohydrate, it may be noted that there is accumulating evidence for the belief that the precursor of lactic acid in muscle is sugar in the form of a hexosephosphoric acid.[62] If this be the case, an important part of the whole metabolism of carbohydrate is associated with a phosphorus combination.

[59] W. B. Bloor, *J. Biol. Chem.*, 1916, **24**, 447 ; *A.*, 1916, i, 450 ; A. Knudson, *ibid.*, 1917, **32**, 337 ; *A.*, i, 136.

[60] N. Fiessinger and R. Clogne, *Compt. rend.*, 1917, **165**, 730 ; *A.*, i, 50.

[61] I. Lifschütz, *Biochem. Zeitsch.*, 1917, **83**, 18 ; *A.*, i, 51.

[62] G. Embden and F. Laquer, *Zeitsch. physiol. Chem.*, 1917, **100**, 181 ; *A.*, 1917, i, 674.

It would be a great mistake, moreover, to suppose that the synthesis of hexosephosphoric acid during the cell-free alcoholic fermentation of sugars is a phenomenon remote from those we are considering.

Since the important observations of Harden and Young first directed attention to this fundamental phenomenon in 1905, much work has been done in connexion with it, and there are some recent papers to be noted. The composition attributed to the hexose-phosphoric acid by the above authors, $C_6H_{10}O_4P(PO_4H_2)_2$, and the fact that it yields lævulose on hydrolysis, have been confirmed.[63] The previously known circumstance that, although the substance is formed under the influence of yeast juice, living yeast cells do not ferment it, has been shown to remain true even when added co-ferment and artificial activators are supplied. Moreover, whilst dried yeast, or cell-free yeast juice, in the presence of sugars esterifies added phosphates almost quantitatively, it is stated that the living cells, even when toluene has been added, may esterify only some 8 per cent. of the added phosphate. These facts have led to the suggestion that the formation of the hexose-phosphate in cell-free or dead cell fermentations is a "pathological" process.[64] This suggestion seems to me unjustifiable and against the weight of evidence. It is far more reasonable to suppose that the whole question is one of cell permeability. In the experiments, which gave so small an esterification of phosphates, it is possible, more-over, that the excess of toluene used was deleterious. Again, in all work with yeasts, the particular strain chosen and its previous history must always be considered.[65] It is stated, for instance, that certain yeasts when weakened by nitrogen starvation fail to esterify phosphates in the presence of dextrose, but nevertheless esterify them when lævulose is supplied.[66] Other experiments, moreover, have shown that when living yeast cells are acting on a mixture of dextrose and phosphates, whilst there may be little synthesis in the earlier stages of the fermentation, the combination of hexose and phosphoric acid occurs rapidly during later stages.[67] In this con-nexion, it is very interesting to learn that an artificial sucrose-phosphoric acid is hydrolysed, and its sugar fermented, by living yeast cells.[68] This seems to me to show that cell permeability plays an important part in these phenomena.

[63] C. Neuberg, E. Färber, A. Levite, and E. Schwenk, *Biochem. Zeitsch.*, 1917, **83**, 244 ; *A.*, i, 91.   [64] *Idem, loc. cit.*

[65] H. Euler, *Biochem. Zeitsch.*, 1918, **86**, 337 ; *A.*, i, 329.

[66] H. Euler, H. Ohlsen, and D. Johansson, *ibid.*, 1917, **84**, 402 ; *A.*, i, 149.

[67] H. Euler, O. Svanberg, G. Hallberg, and K. Branding, *Zeitsch. physiol. Chem.*, 1917, **100**, 203 ; *A.*, i, 54.

[68] K. Djenab and C. Neuberg, *Biochem. Zeitsch.*, 1917, **82**, 391 ; *A.*, 1917, i, 680.

The Biochemical Degradation of Dextrose.

Many references have been made in these Reports to investigations dealing with the intermediary metabolism of dextrose in the animal body and with the problem of determining successive stages in its degradation. During the past year, work on the subject has been more or less quiescent. To one statement, however, I should like to direct attention.[69] If dextrose solutions are, under suitable conditions, perfused through the pancreas, the optical dextrorotation of the perfusates is said to be diminished without any alteration in their reducing power. Osazones from such perfusates have a lower melting point than glucosazone. It is supposed that these changes represent a preparation of the sugar for normal utilisation. Such experimental results may represent nothing more than the occurrence of condensation to a polysaccharide, on lines already suggested by the work of Levene and Meyer and by that of Lombroso.[70] Whether this condensation really involves the formation of a phosphoric acid complex seems, by the way, not yet to have been considered. What, however, is of special interest in the recent work under notice is the circumstance that, unlike dextrose, lævulose is not affected by perfusion through the pancreas. Now lævulose is certainly well utilised in the body, and, under certain diabetic conditions, better utilised, or at least more easily converted into glycogen, than dextrose itself. There seems, indeed, to be just the suggestion that lævulose is not affected by the pancreas, because it is already available for utilisation. One thinks, at any rate, of points discussed in the preceding section—of the fact that the carbohydrate in hexose-phosphate, although produced by yeast juice from dextrose, yields lævulose on hydrolysis; of the circumstance that a weakened yeast, unable to esterify dextrose, can yet deal with lævulose. There appears, indeed, to be an indication that in certain circumstances, at any rate, the protoplasm can grip the ketose structure more readily than the aldose structure, and that preparatory processes may be concerned with the conversion of the latter into the former.

It is certainly undesirable that those who seek for information concerning animal metabolism should ignore the facts won from the study of the lower organisms. They may not be susceptible of direct application, but they may often afford suggestion and guidance. I propose to remark on some further studies of yeast which can be logically considered after those dealt with in the last section.

[69] A. H. Clark, *J. Exp. Med.*, 1917, : **6**, 721 ; *A.*, i, 139.

[70] *Ann. Report*, 1916, 214.

Although probably no one doubts that a three-carbon compound of some sort is an early intermediate product in the process of alcoholic fermentation, lactic acid, since the work of Slator, has been held to be out of court in this connexion. Only in the presence of some added reducing substance (hydrogen acceptor), such as methylene-blue, are the conditions given for any appreciable production of alcohol from this acid. The reductase of yeast can with this assistance convert the lactic acid into acetaldehyde, which may itself suffer reduction to alcohol. In any case, the results of quantitative studies are against the view that lactic acid is a normal intermediary product.[71] On the whole, it seems that the trioses must also be ruled out. Neither glyceraldehyde nor dihydroxyacetone undergoes fermentation with yeast. It has been claimed, indeed, that the synthetic phosphoric ester already discussed contains a triose group as well as a hexose group, but the evidence is far from conclusive.[72] Trioses yield methylglyoxal on distillation, whilst hexose-phosphoric acid yields none.

On the other hand, the evidence to show that pyruvic acid is a normal intermediary in the production of alcohol seems to be strengthening, even although we are ignorant of what stands between it and the hexose molecule. The case in its favour clearly grows stronger with the proof that acetaldehyde is formed by yeast in really considerable amounts, since it is well known that the carboxylase of yeast rapidly converts pyruvic acid into aldehyde. By growing yeast in the presence of sodium sulphite, the proof is obtained.[73]

The formation of pyruvic acid from sugar involves the removal of hydrogen under the influence of the yeast reductase, and for the continuance of this stage of the degradation an acceptor for the hydrogen is required; this acceptor has been assumed to be acetaldehyde itself, of which, as soon as it is formed, a moiety is converted straightway into alcohol. From one molecule of sugar, therefore, any process involving partial arrest at the aldehyde stage could yield at the most one molecule of the aldehyde. Of the amount to be expected on this view, as much as 75·45 per cent. has been obtained by fermentation in the presence of sodium sulphite.

Of the importance of the aldehyde stage there can therefore be no doubt, but if we accept the above view of fermentation as a whole, we have to recognise that acetaldehyde, as well as being the

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[71] Compare A. Lebedev, *Biochem. J.*, 1917, **11**, 189; *A.*, i, 149.

[72] A. Lebedev, *ibid.*, 1918, **12**, 87; *A.*, i, 364.

[73] C. Neuberg and E. Reinfurth, *Biochem. Zeitsch.*, 1918, **89**, 365; *A.*, i. 517.

immediate precursor of the alcohol, has to initiate by its presence the production of the very substance from which it itself takes origin. It is clear, therefore, that some minimal amount of pre-formed aldehyde must be present from the first in any fermenting system. There at once occurs to the mind a particular possibility.

Since the pioneer observations of Harden and Young, it has become fully established that when yeast juice is filtered or dialysed, a factor necessary for fermentation passes into the filtrate or dialysate, the residue being incapable of fermenting sugar until that factor is restored. This factor is the so-called co-ferment. Is acetaldehyde this co-ferment, or is it present as a constituent of the co-ferment system?

The presence of pyruvic acid would have identical significance, because the carboxylase of yeast is not removed by filtration or dialysis, so that the residue can still convert the acid into the aldehyde.

It has been known for the last three years[74] that the addition of small amounts of pyruvates accelerates fermentation by macerated yeast. It is asserted,[75] however, that neither yeast-juice nor zymin (acetone yeast), when once deprived of its co-enzyme, is reactivated by pyruvates when these are added alone, not even when a proper supply of phosphates is present. Reactivation calls, it is said, for a mixture of keto-acids or their salts. This statement has always been difficult to understand, and to judge from recent work it does not seem to be true,[76] although still maintained by its originator.[77] Zymin rendered inactive by thorough washing is, as a matter of fact, readily activated by potassium pyruvate in the presence of a suitable concentration of potassium phosphate. Acetaldehyde in similar circumstances also activates, and a great number of other aldehydes have been shown to do the same.[78] Incidentally, it is interesting to know that potassium or ammonium phosphate must be supplied in all cases; sodium phosphate is quite ineffective.[79]

There would seem from the facts so far before us to be good grounds for the belief that what is washed away during the in-activation of yeast preparations consists of such amounts of pyruvates or acetaldehyde as are normally present in the yeast.

[74] M. Oppenheimer, *Zeitsch. physiol. Chem.*, 1915, **93**, 235; *A.*, 1915, i, 358.

[75] C. Neuberg and E. Schwenk, *Biochem. Zeitsch.*, 1915, **7**, 135; *A.*, 1915, i, 1045.

[76] A. Harden, *Biochem. J.*, 1917, **11**, 64; *A.*, 1917, i, 501.

[77] C. Neuberg, *Biochem. Zeitsch.*, 1918, **88**, 145; *A.*, i, 469.

[78] C. Neuberg, *loc. cit.*

[79] A. Harden, *Biochem. J.*, 1917, **11**, 64; *A.*, 1917, i, 501.

The "co-ferment" would thus represent no more than these remainders from previous activity. In deciding this point, however, quite recently won facts of no small interest must be taken into account. It has now been conclusively shown [80] that extracts of animal tissues can with equal efficiency take the place of the co-ferment preparations made from yeast itself. If yeast maceration juice is filtered, and the material on the filter thoroughly washed, the residue, by itself entirely inactive, ferments sugar freely after the addition of a boiling-water extract of minced muscle. The activating substance thus demonstrated in muscle is found in almost all animal tissues, although absent from blood serum. Its chemical properties resemble precisely those associated with the co-enzyme of yeast itself, and the course of fermentation under the influence of a muscle extract is strictly comparable with what is observed when the co-enzyme from yeast is employed.

It is stated that the substance, present in both yeast and muscle, which acts as the co-enzyme of the fermentation acts also as a respiratory catalyst.[81] If chopped muscle is thoroughly washed, its power to absorb oxygen may be reduced nearly to zero. It is restored, however, on the addition of boiled aqueous extracts of either yeast or muscle. The oxygen-consumption of washed yeast is also greatly increased by such extracts, whether their source be yeast itself or muscle. These observations may be held to support the old hypothesis that the earlier phases in the processes of fermentation and respiration, respectively, are closely related, and suggest perhaps that the conversion of sugar into a three-carbon derivative, which can then be fermented (yeast) or oxidised (muscle), is a process in which the same co-ferment assists.

There is no question at all as to the trustworthiness of these statements in so far as they relate to the power of the animal tissue extracts to take the place of the yeast co-ferment in alcoholic fermentation. The experiments are quite easy to repeat. How far they ought to modify our attitude towards the view that the co-enzyme of yeast consists of pyruvic acid or acetaldehyde it is difficult to decide. Both these substances have been supposed to be intermediate products in animal metabolism, although proof of the supposition is lacking.[82] They certainly do not accumulate to any appreciable extent in animal tissues, and the amounts contained in muscle extracts which are effective in stimulating fermentation must be infinitesimal. This circumstance does not, it is true, decide against them as possible activators. We have known for

[80] O. Meyerhof, *Zeitsch. physiol. Chem.*, 1918, **101**, 165 : **102**, 1 ; *A.*, . 242, 464.

[81] O. Meyerhof, *loc. cit.*   [82] See *Ann. Report*, 1914, 204.

some time, it should be noted, that a hydrogen acceptor, necessary for the reduction of methylene-blue by muscle, can be washed from the tissue by saline solutions, and can then be replaced by acetaldehyde. It can also, however, be replaced by other substances.[83]

The co-enzyme effect may, after all, be due to other reducing agents in muscle. We already know that acetaldehyde, even if the normal hydrogen acceptor in fermentation, is not specific in that function; other aldehydes are effective, and so perhaps may be other types of reducing agents.

The statements mentioned above with regard to the stimulation of the respiratory process recall others long familiar. The latter were based on experiments from which it appeared that tissues which have been kept for some hours after death, and in which the oxidative processes are gradually becoming less, can be reactivated by the addition of aqueous extracts of various fresh tissues. These older experiments have received damaging criticism, but I think the more recent ones, as well as having more precise significance, are based on greatly superior technique, and their results point in an interesting way to the existence of closely related chemical mechanisms in animal and vegetable cells.

Some Tissue Constituents.

Work at the Rockefeller Institute seems to be satisfactorily clearing up the nature and the mode of linking of the amino-sugars in mucins and mucoids. It is thirty years since C. T. Mörner announced the presence of chondroitin-sulphuric acid in cartilage. The proof that a conjugated sulphuric acid compound containing an amino-sugar is a constituent of a connective tissue aroused great interest at the time, as well it might, but until very recently little progress had been made towards a closer characterisation of this type of tissue constituent. It is now established that two examples exist: chondroitin-sulphuric acid and mucoitin-sulphuric acid respectively. The former yields chondrosamine (d-lyxohexosamine) on hydrolysis; the latter, on the other hand, yields *mucosin*, a disaccharide ($C_{12}H_{21}O_{11}N$), which breaks down into glucosamine, and glycuronic acid. The chondroitin compound is contained in the aorta and sclera, the mucoitin compound in mucins from various tissues—the vitreous humour, the cornea, and the gastric mucosa, for instance. It is present also in ovomucoid and in ovarian cysts.[84]

[83] A. Harden and H. MacLean, *J. Physiol.*, 1915, **9**, 330.

[84] P. A. Levene and J. López-Suárez, *J. Biol. Chem.*, 1918, **36**, 105 : A., i, 554.

Most satisfactory is it to get definite information as to the relation of the iodine in the thymus gland. From the hydrolytic products of the proteins of the gland an iodine derivative of the indole (tryptophan) nucleus can be separated which, as stated in the last Report, has a physiological action akin to the physiological activities of the gland itself. Its constitution is now stated[85] to be the following:

$$\begin{array}{c} \text{I} \quad \text{I} \\[2pt] \text{HI} \quad \text{C·CH}_2\text{·CH}_2\text{·CO}_2\text{H} \\ \text{HI} \quad \quad \text{:O} \\ \quad \text{H} \quad \text{NH} \end{array}$$
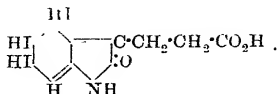
Physiological chemists cannot fail to be interested in the discovery of hydrocarbons in the liver of fishes. When this was first announced, it seemed likely that such substances might well be formed by the elimination of carbon dioxide from fatty acids under the influence of some enzyme of the carboxylase type. In view of their constitution, this cannot be true. An unsaturated hydrocarbon, squalene, $C_{30}H_{50}$, was first separated[86] from shark liver oil in 1915, and has now been further studied.[87] A saturated hydrocarbon, $C_{18}H_{38}$, seems, in some specimens of the oil, to be associated with squalene. Spinacene, first observed in 1915[88] in oils from the livers of species belonging to the *Spinacidæ*, has now been more fully examined, and has been found to have the structure of a terpene.[89] We have to think of it, and, maybe, also of squalene, for they are probably allied if not identical, as related in metabolism to cholesterol and the bile acids. rather than with fats.

There is no doubt that, in the future, comparative studies in physiological chemistry will throw much light on processes as they occur in mammals and on the meaning of many tissue constituents. It is a far cry from the fish-liver hydrocarbons, but I think the same point is illustrated by such a fact as that a substance, helicorubin, found in the "bile" of the snail (*Helix pomatia*), may be looked on as an "embryonic" or "ancestral" form of hæmoglobin. This substance has received fresh attention lately,[90] and there can be no doubt of its close relations with blood pigment. A fascinating phenomenon discovered in comparative physiology is found in the

[85] E. C. Kendall, *Endocrinology*, 1918, **2**, 81 ; *A.*, i, 560.

[86] M. Tsujimoto, *J. Ind. Eng. Chem.*, 1916. **8**, 889 ; *A.*, 1916, i, 786.

[87] M. Tsujimoto, *ibid.*, 1917, **9**, 1098 ; *A.*, i, 89.

[88] A. C. Chapman, *T.*, 1917, **111**, 56.

[89] A. C. Chapman, *ibid.*, 1918, **113**, 458.

[90] C. Dhéré and G. Vegezzi, *J. Physiol. Path. gén.*, 1917, **44**, 53 ; *A.*, i, 85.

influence of a hormone on the colour of the skin of an animal. It is said, at least, that black pigment cells in the epidermis of Philippine house lizards never, as in other cases, expand or contract, but when these creatures become, for instance, light-coloured on white surroundings, the bleaching is due to the discharge of something into the blood. Adrenaline when artificially injected is capable of producing the effect, and also bleaches the pigment *in vitro*.[91] Very interesting, again, are recent studies[92] of the luminescence of various insects and other animals, showing its dependence on the interaction of two substances, one possibly an oxydase, in the presence of oxygen. I have taken these few references to observations on the lower animals quite at random.

F. GOWLAND HOPKINS.

[91] E. G. Ruth and R. B. Gibson, *Philippine J. Sci.*, 1917, 12, [B], 181.

[92] E. N. Harvey, *Amcr. J. Physiol.*, 1916, 41, 449, 454; 42, 318, 342, 349, A., 1917, i, 365.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

THE distinguishing feature of the year 1918 from the point of view of the agricultural chemist was the urgent need to increase food production under a growing shortage of fertilisers and feeding-stuffs. The problem before him was twofold: to increase supplies of these essential commodities and to advise farmers how best they might make use of the limited amounts at their disposal. This is not the place to discuss the methods adopted or the results; both are described in the Report on Agricultural Chemistry issued by the Society of Chemical Industry. Following established custom, this Report deals primarily with advances in our knowledge of agricultural chemistry rather than with applications of known principles.

The Soil.

The basis of the farm resources is the soil. Considered in relation to plant growth, it may be regarded as a highly porous mass composed of solid mineral fragments intimately mixed with decomposing plant and animal residues. It possesses all the attributes of colloids, such as powers of adsorption, retention of water, etc., to so marked an extent as to suggest that its particles are coated with a gel, which might well be formed of silica, alumina, iron oxide, and other substances; in contact with all this is the soil moisture, which is presumably saturated with all the soluble substances in the soil.

This soil moisture is of great importance in crop production. All investigators agree that it constitutes the nutrient solution for the plant. In this country it is usually considered to fluctuate so much in composition with rainfall, manuring, and soil treatment that it has proved unattractive to investigators. In the United States, however, it is regarded by many as being sufficiently definite to justify close study, and it has evoked a considerable bulk of work. The soil solution was first brought into prominence in

1903, when Whitney and Cameron published their striking hypothesis that it is a saturated solution of the soil minerals in equilibrium with them, and therefore of constant composition in all soils, since all are made up of the same minerals.

A series of papers has recently been published from the Californian Agricultural Experimental Station which throws considerable light on the subject. The depression of the freezing point of the solution in the soil was determined under varying moisture conditions. This had already been done by Bouyoucos and McCool at Michigan [1] as a means of expressing variations in the concentration of the soil solution. The depressions vary with the moisture content of the soil, but not in a direct ratio; the variation is such as to suggest that a certain fraction of the total water is not subject to freezing, and apparently it is so combined that it does not form an effective part of the soil solution. This assumed fraction is called the "unfree water." Accepting this method and its consequent assumption, the Californian investigator [2] finds that the soil solution is neither saturated nor constant in composition. Thus Whitney's fundamental assumption is controverted. Storage in a bin greatly increased the soluble matter in the soil; washing with water reduces it to a low level, where it remains for a long time. Cropping the soil also reduces the soluble matter. All these propositions are acceptable, and, indeed, were proved by direct chemical determinations.[3] Various soils were set up in large vessels and subjected to definite, but different treatments; some were cropped and some uncropped. Frequent samples were drawn for analysis of the water extract, which is supposed to reflect the composition of the soil solution. An enormous amount of analytical work was involved, but it has long been recognised [4] that continuous curves offer the only safe basis of comparison in soil investigations. A great mass of detail is thus obtained which is difficult to discuss adequately. In general, however, the graphs are somewhat similar for cropped soils, but show striking differences for uncropped soils. The more fertile uncropped soils had a higher concentration than the infertile ones—again in opposition to the old hypothesis of Whitney and in accordance with the results obtained at Rothamsted by Hall, Brenchley, and Underwood—but in between these extremes there came intermediate soils, in which the concentration of the solution was not clearly connected with productiveness.

[1] G. J. Bouyoucos and M. M. McCool, *Michigan Tech. Bull.*, 24, 1916.
[2] D. R. Hoagland, *J. Agric. Res.*, 1918, **12**, 369.
[3] G. R. Stewart, *ibid.*, 311.
[4] Compare E. J. Russell and H. B. Hutchinson, *J. Agric. Sci.*, 1909, **3**, 131.

These investigations are further discussed and extended by Burd,[5] who sets out the results in terms of the amounts of solutes extracted by the crop from the soil, and not in terms of concentration in the soil. This was done by harvesting portions of the crop on different dates and determining the soil constituents present. Knowing also the amount of water-soluble material in the soil, he is able to determine how long this supply would last assuming the daily draft continued at a constant rate and that the whole of the soluble material could be taken by the plant. Making these assumptions, it is found that there were never less than nine days' supply of nitrate or twenty-four days' supply of phosphate in the soil.

Now it is distinctly remarkable that even poor soils should always contain sufficient nitrate, phosphate, etc., in the soil solution to supply the plant for at least nine days, because it is notorious that additions of nitrates, phosphates, etc., do cause increased growth. This, indeed, is the old difficulty urged against the original Whitney hypothesis, and the author finds no way out except the suggestion that in infertile soils the plant is unable to absorb all the potentially soluble material.

When a train of argument leads to difficulties of this sort, it is well to go back and re-examine the fundamental assumptions; in this case there are two, namely, that extraction of the soil with water removes nothing beyond what is soluble in the natural soil moisture, and that the plant can take the whole of the potentially soluble material from the soil. Neither assumption is necessarily sound, and indeed the second is inherently improbable, for soil has powerful absorbent properties and would be far more likely to come into equilibrium with another absorber like a plant—an equilibrium, moreover, which would only slowly be disturbable—than to yield up the whole of its supply on demand.

Continuing his argument, however, the author proceeds to add the quantities of nutrients present in a "good crop" to those found in the cropped soil, and then compares the result with the amounts found in uncropped soils. In the case of nitrates, there is a deficit; this is the usual experience, and implies that the growth of the crop in some way depresses nitrification. In the case of phosphates, however, there is an excess; one may suppose that the growth of the crop has somehow promoted the solution of otherwise insoluble phosphates, etc., or else that the soluble material extracted from the uncropped soil does not represent all that is soluble, but only the fraction that is actually dissolved; and, further, that in good soils the water-soluble material is replaced as fast as the plant

[5] J. S. Burd, *J. Agric. Res.*, 1918, **12**, 297.

absorbs it. In the case of phosphates, however, the author could find no evidence of greater power or rapidity of renewal of soluble phosphates in good than in poor soils; in both cases renewal must have been rapid, because the quantity found in the solution showed no reduction with the growth of the crop.

Speaking generally, the results are at variance with those obtained by Whitney and in agreement with those obtained at Rothamsted. The controvertible point still remains whether a poor soil can be said "to be able to furnish adequate amounts of all solutes at the most critical periods." It may well be that a re-examination of the problem, having regard to the phenomena of soil adsorption, would lead to interesting results.

Turning to the solid phase, this, as already stated, shows marked colloidal properties, and, indeed, no studies of soil problems can now be regarded as satisfactory which ignore this fact. A summary of these properties and a discussion of their bearing on soil problems have appeared in the form of a monograph.[6]

One of the most remarkable properties shown by the smallest clay particles is that they become flocculated in the presence of acids and dissolved salts and deflocculated in the presence of alkalis. This phenomenon has generally been regarded as electrical; clay was supposed to be an electronegative colloid, the charge on which is neutralisable by electropositive ions. An alternative chemical hypothesis has, however, been put forward, and flocculation attributed to a combination of clay with the flocculant and the solute, whereby the aggregation of molecules increases so much that they lose the power of Brownian movement and soon settle.[7]

Another important property commonly attributed to colloids is absorption. There is, however, a chemical school that ascribes this property to the supposed presence of the specially reactive minerals known as zeolites. It is admitted that no mineralogical evidence has been obtained of the existence of zeolites in soils, but it is claimed that the observed phenomena warrant the assumption. If it is conceded that zeolites occur in the soil and that the absorption and power of exchanging bases shown by zeolites is chemical,[8] then the phenomena of absorption and interchange of bases in soils may be chemical also. This view finds favour among the Russian investigators,[9] whilst the physical adsorption view is more

[6] P. Ehrenberg, "Die Bodenkolloide" (Steinkopf), 2nd ed., 1918.

[7] S. U. Pickering, *Proc. Roy. Soc.*, 1918, **94**, [A], 315.

[8] As claimed by V. Rothmund and G. Kornfeld, *Zeitsch. anorg. Chem.*, 1918, **103**, 129; *A.*, ii, 315, in opposition to G. Wiegner's view that it is physical, *J. Landw.*, 1912, **60**, 197; *A.*, 1912, ii, 981.

[9] K. K. Gedroitz, Reprints, *A.*, i, 519 and ii, 364.

commonly accepted in this country, in the United States, and in Germany.

Under certain conditions, a precipitate of ferric oxide or other substance is formed in the soil at a certain depth below the surface. When this becomes continuous, it cements the soil particles into a layer of rock 5—7 cm. in thickness, known as a pan, which causes considerable damage to crops by interfering with free movement of water and unduly restricting root growth. The precipitation is now regarded as a colloidal phenomenon, a change from a sol to a gel. Further observations have been made on the precipitation of ferric oxide solutions.[10]

Yet another property of soil claimed as a colloidal phenomenon is acidity. Certain soils turn blue litmus red: it is assumed, therefore, that these have the power of preferential adsorption, taking up the basic ions more readily than the acidic, and thereby changing the colour of the indicator. The chemical school, however, stoutly maintains the presence of substances of acid reaction in the soil, although with much controversy as to whether these are true acids or salts of iron and aluminium. The believers in true acids are faced with the difficulty that no undeniable acid has ever been isolated from the soil except in very minute amounts, but they have used various methods to demonstrate their presence—measurement of the hydrogen-ion concentration, rate of inversion of sucrose, liberation of iodine from mixtures of potassium iodide and iodate, etc. These all give positive indications, but unfortunately in quantitative experiments they do not agree among themselves, nor do they show any relationship to the litmus test[11] or the amount of lime or calcium bicarbonate required to "neutralise" the soil, that is, to leave an excess of unchanged lime.[12]

The determination of the hydrogen-ion concentration has been carried out mainly in the United States. Remembering how complex is the soil solution, one cannot help asking whether the method is really applicable and whether investigators are justified in writing down definite P_H values. A critical and fundamental investigation into the validity of the method seems required. In the meantime, measurements are accumulating; for normal soils the figures vary from true neutrality to well-marked true acidity. Manuring the soil with ammonium sulphate or potassium sulphate

[10] M. Neidle, J. Amer. Chem. Soc., 1917, 39, 2334; A., ii, 45.

[11] L. J. Gillespie and L. E. Wise, J. Amer. Chem. Soc., 1918, 40, 796; A., i, 368.

[12] D. R. Hoagland and L. T. Sharp, J. Agric. Res., 1918, 12, 139.

increases the value, the former being more potent than the latter: sodium nitrate slightly reduces it; superphosphate has no effect.[13]

The rate of inversion of sucrose has also been used in the United States as a measure of the hydrogen-ion concentration, but this method involves the assumption that the hydrogen ion is the only thing that can invert sucrose.[14] The results do not agree with those obtained by the direct electrical or indicator methods; the authors therefore suppose that these methods simply measure the soluble, but not the total acidity. They consider that an insoluble acid must operate in the soil, because the amount of inversion increases with the quantity of soil used, which could not be the case if the dissolved portion alone was active. As further evidence of the action of an insoluble acid, the authors adduce the fact that inversion still goes on even in the presence of sufficient lime to make the solution alkaline. Again the fundamental assumption is open to question, and it will be asked whether, in view of the lime result, one can still assume that inversion is brought about only by the hydrogen ion. In these matters, the agricultural chemist necessarily relies for guidance on the physical chemist.

It has been shown that the passage of carbon dioxide through a soil increases its acidity, as also does the growth of a crop. It is suggested, therefore, that the liberation of the hydrogen ion is due to carbon dioxide generated within the soil.[15]

Another explanation of the phenomena of acidity is that it arises from the hydrolysis of salts of iron and aluminium formed by addition of other salts to the soil. The acidity of certain glacial soils has been attributed to the "hydrolytic ratio" between the salts of the alkaline earth metals on the one hand, and those of iron and aluminium on the other.[16]

Further, it has been argued[17] that the toxic effect of "acid" soils cannot in any case be due to true acids even if they are present, because acids added to the nutrient solution in water cultures affect barley and rye similarly, whilst extracts of acid soils affect them differently. Therefore acid soil extracts contain something not present in acid nutrient solutions; on testing, they were found to contain aluminium. The effect of aluminium salts on plant growth was examined and found to

[13] J. K. Plummer, *J. Agric. Res.*, 1918, **12**, 19.. The method was introduced by L. J. Gillespie, *J. Washington Acad. Sci.*, 1916, **6**, 7; *A.*, 1916, i, 303.

[14] F. E. Rice and S. Osugi, *Soil Sci.*, 1918, **5**, 333; *A.*, i, 520.

[15] H. A. Noyes and L. Yoder, *ibid.*, 151.

[16] C. H. Spurway, *J. Agric. Res.*, 1917, **11**, 659; *A.*, i, 152.

[17] B. L. Hartwell and F. R. Pember, *J. Amer. Soc. Agron.*, 1918, **10**, 45.

resemble that of the acid soil extract. If these observations are well founded, the conclusions drawn by the authors seem to be irresistible. The hydrogen-ion measurements may indicate the presence of free acid in acid soils. assuming always the validity of the method. but the plant test is final; the importance of these observations lies in the fact that they make the appeal direct to the plant.

Whatever the cause of soil acidity, it can be remedied by additions of lime. In practice, this is highly important, because acid soils are infertile for most farm crops, whilst after neutralisation they may become quite productive.

Considerable areas in this country need lime. and cases are not infrequently recorded [18] where infertile patches in a field are found to be acid and almost free from carbonates, whilst the rest of the field, which is still fertile, is not acid and still contains carbonates, although sometimes only little.

Besides neutralising soil acidity, lime has other effects less easy to explain.. Its action on the water-soluble nutrients is found to differ with the soil and the previous treatment.[19] Thus in two soils the water-soluble potash was increased as a result of liming; in two it was decreased; in four soils the soluble magnesia content was increased; in one decreased; sometimes the soluble phosphate was increased and sometimes it was not. No explanation is put forward of these phenomena, nor is any correlation attempted with other chemical properties of the soils in question.

The complex nature of the action of lime may be further gauged by the difficulty of ascertaining what becomes of it in the soil. Hager claims [20] that only a small part of the added quicklime appears as carbonate, the remainder being absorbed by soil constituents. The power of absorption appears to be related to the amount of clay present, the process here presumably being physical. but it is also considered that unsaturated compounds are present with which the lime reacts chemically.

There are. however, large areas of cultivated land that are acid but so far from any source of lime as to preclude the possibility of neutralisation on a large scale. Corville suggested some years ago [21] that a system of "acid agriculture" might be developed in such cases by means of a suitable rotation of acid-resistant crops. Inasmuch as a leguminous crop would be essential for the maintenance of the nitrogen supply, recent attempts have been

[18] E. J. Russell, *J. Bd. Agric.*, 1918, **25**, 1102.
[19] A. W. Christie and J. C. Martin, *Soil Sci.*, 1918, **5**, 383.
[20] G. Hager, *J. Landw.*, 1917, **65**, 245 *:; ,1.,* i, 247.
[21] *U.S. Dept. of Agric. Bull*, **6**, 1913.

made to study the effect of acidity on the nodule organism.[22] Other
soil bacteria were also included. The soja bean was found to be
a suitable crop, growing and fixing nitrogen (through the agency
of the nodule bacteria) even in the presence of soil acidity. The
other bacteria were considerably affected, however. Those grow-
ing on gelatin plates were greatly increased in number when
sufficient calcium carbonate was added to bring about neutral-
isation (using the Veitch method of indicating neutrality), and
still further increases were obtained when phosphates were added
to the neutralised soil. The rates of ammonification and of nitrifi-
cation were affected by addition of calcium carbonate before the
neutralisation point was reached, and not much afterwards, in
which respect they differed from the bacterial numbers; non-
symbiotic nitrogen fixation was also stimulated, especially in the
presence of phosphate. The general conclusion in regard to non-
leguminous plants is that those capable of assimilating ammonia
can flourish in an acid soil, whilst those dependent entirely on
nitrates cannot.

The most characteristic soil constituent is the organic matter
derived from residues of plants and animals, and its most significant
property is that it is perpetually undergoing decomposition, with
ultimate formation of carbon dioxide, water, ammonia, and various
inorganic salts.[23] Several agencies are involved, bacteria, moulds,
enzymes, etc., and, as the changes go on at low temperature,
numerous intermediate products are formed. The decomposition
is an important factor in soil fertility, because the resulting nitrates
are essential to plant growth; the process may, indeed, be regarded
as the manufacture of plant nutrients in the soil.

The original organic substances added to the soil in the plant
residues include carbohydrates such as starch, sugar, cellulose, the
pentosans, gums, etc., proteins, nucleoproteins, fats, waxes, and
numerous other substances. The number of possible intermediate
products is, of course, enormous, and the list of known soil con-
stituents is continually being extended; this year, two more com-
pounds have been isolated, benzoic acid and p-hydroxybenzoic
acid; the quantity of the latter was distinctly appreciable, amount-
ing to 22 parts per million of soil; there was less than one-tenth
this amount, however, of benzoic acid.[24] The real importance
of the search for soil constituents will be revealed only when the

[22] F. E. Bear, *Soil Sci.*, 1917, **4**, 433; *A.*, i, 206.

[23] A detailed comparison has been made of the inorganic composition of
the original plant and that of the peat to which it has given rise. See C. F.
Miller, *J. Agric. Res.*, 1918, **13**, 605.

[24] E. H. Walters, *J. Amer. Chem. Soc.*, 1917, **39**, 1778; *A.*, i, 152.

process of formation and the functions of the compounds are understood.

The main interest at present lies in the mechanism of the process, for until this is known it is difficult to interpret the chemical data. Chemical and biological investigations should go on side by side, but for the time being the biologists have outstripped the chemists. In view of the general similarity both of the initial products and of the conditions of decomposition in different soils, it is reasonable to anticipate similar intermediate products. In last year's Report some evidence was adduced on this important fundamental point; the nitrogen compounds revealed by the Van Slyke method were said to be much the same in all soils examined.[25] It has since been shown, however, that this method does not apply to soils, being vitiated by the ferric salts formed from the soil during the hydrolysis. This is an unfortunate setback, but it illustrates the great difficulties under which the soil investigator labours. Progress is largely dependent on the introduction of new methods and conceptions from pure chemistry, but at every stage the closest scrutiny is necessary to ensure that the proposed method is really valid.

Broadly speaking, investigations proceed in two directions: the actual processes in the soil are as far as possible traced out, and information is accumulated as to the way in which given types of compounds decompose in the soil.

Aliphatic nitrogen compounds are more easily converted into ammonia than aromatic amino-compounds, and these in turn more rapidly than aromatic imino-compounds.[26] Thus the compounds tested broke down to ammonia in the following order: acetamide most readily, then leucine, tyrosine, benzamide, acetanilide, and finally benzanilide. Another investigator[27] has shown that di-cyanodiamide does not decompose in the soil, whilst cyanamide rapidly breaks down, a fact which may throw some light on its constitution.

The efforts to trace out the actual processes in the soil have met with considerable success. Two general types of change are known: a degradation, whereby protein breaks down to form ammonia, and a remarkable constructive change, in which gaseous nitrogen is converted into protein. About the steps in this synthesis nothing is known, but the conditions under which it takes place have been examined in the Rothamsted laboratory.[28]   A

[25] *Ann. Report*, 1917, 203.

[26] K. Miyake, *J. Amer. Chem. Soc.*, 1917, **39**, 2378 ; *A.*, i, 91.

[27] G. A. Cowie, *J. Agric. Sci.*, 1918, **9**, 113.

[28] H. B. Hutchinson, *J. Agric. Sci.*, 1918, **9**, 92.

source of energy is obviously necessary; this is supplied by the decomposable carbohydrates. When plant residues were added to the soil, fixation of gaseous nitrogen was observed amounting to 9 milligrams per gram of substance added. Other necessary conditions are suitable temperature, presence of phosphates and of calcium (or magnesium) carbonate. This process is wholly beneficial. In addition, another synthetical process was observed starting from nitrates; this is harmful, because it results in the temporary withdrawal of nitrate from the supply available for the plant. In practice, therefore, the carbohydrate or plant material would be added in autumn, when the temporary withdrawal of nitrate does not seriously affect farm crops and the fixation process has time to take place before spring. The organisms concerned, *Azotobacter*, are widely distributed.[29]

The decomposition of sulphur compounds with final production of sulphates has received some attention in the United States, especially the relations of " sulphofication " to other soil decompositions.[30]

It will surprise no organic chemist that during the degradation of organic compounds in the soil there is a considerable production of a black, non-crystalline material soluble in sodium hydroxide and largely precipitated by acids. Formerly, this so-called humus was supposed to be an intermediate product in the production of nitrates, and therefore it was estimated so as to give a measure of the potential fertility of the soil.[31] Several investigators of recent years have shown that it is not related to fertility, but is, as might be expected, a by-product rather than a main product. Further evidence is now offered from the soils in orange groves.[32]

The decomposition is brought about by bacteria, fungi, and other organisms, but their relative part is unknown. Indeed, the evidence in favour of activity of fungi is by no means unexceptionable. It has been argued, for instance, that fungi must operate in the soil, because approximately equal amounts of carbon dioxide are evolved from sterilised soil whether moulds or bacteria are

[29] P. L. Gainey, *J. Agric. Res.*, 1918, **14**, 265, found them in 59 per cent. of the soils examined ; in these cases the P_H value was less than 6.

[30] Of papers published this year the following may be mentioned : J. W. Ames and T. E. Richmond, *Soil Sci.*, 1918, **5**, 311. H. C. McLean, *ibid.*, 251 : this deals especially with the oxidation of sulphur by micro-organisms. O. M. Shedd, *J. Agric. Res.*, 1917, **11**, 91 ; *A.*, i, 96 : the effect of sulphur on crops and soils.

[31] New methods of estimation are still devised by ingenious chemists, although the value of the results is no longer generally admitted. See, for example, A. Jakobsen, *Zhur. Optyn. Agron.*, 1916, **17**, 93 ; *A.*, ii, 136.

[32] C. A. Jensen, *J. Agric Res*, 1918, **12**, 505.

introduced.[33] The argument is not really valid, because heating soil is well known to make it suitable to certain types of moulds.

A new method of counting soil protozoa has been devised, making use of the apparatus for counting blood corpuscles; there are now five methods available.[34]

The important part played by bacteria in the decomposition of the organic matter of the soil and the vital importance of the products as plant nutrients have led to careful study of the relationships between soil conditions and bacterial activity. In general, these are the same as the relationships between soil conditions and plant growth, plants and bacteria both being living things and affected similarly by the same biological factors. This similarity has been well brought out in an investigation on the effect of sodium nitrate on the nitrogen transformations in soils.[35] Sodium nitrate increased the numbers of ammonifying bacteria, and in normal soils increased also the amount of decomposition of added protein; in alkali soils, however, there was apparently some rearrangement of the flora, so that the simplified material was assimilated, thereby masking the decomposition effect. Fungi were even more affected than bacteria. The nitrifying and nitrogen-fixing organisms both benefited up to a certain point, beyond which further increases in the amount of sodium nitrate cause a falling off in activity. A more detailed study of the effect on the nitrogen-fixing *Azotobacter* has been made.[36] Small quantities of the nitrates of potassium, sodium, or calcium caused great increases in the numbers of *Azotobacter* in sterilised soil, although not a commensurate increase in the amount of nitrogen fixed. The nodule organism, *Bacillus radicicola*, also increased in numbers after addition of nitrates, but the gain in fixed nitrogen was only slight and there was an actual depression of nodule formation which could not easily be explained.

Moreover, it is shown[37] that in alkali soils the excess of saline matter impairs the vitality of the organisms; after the excess of salts is washed out, however, the organisms act more vigorously. The ammonifying organisms are the most hardy, next come the nitrifying organisms; both these tolerate more salinity than cultivated plants, so that in the washing-out process the activity of the nitrate-forming organisms becomes marked before the soil is yet

[33] R. S. Potter and R. S. Snyder, *Soil Sci.*, 1918, **5**, 359.
[34] A. Itano and G. B. Ray, *ibid.*, 303.
[35] D. A. Coleman, *ibid.*, 1917, **4**, 345.
[36] T. L. Hills, *J. Agric. Res.*, 1918, **12**, 183 ; *A.*, i, 328.
[37] J. H. Barnes and B. Ali, *Agric. J. India*, 1917, **12**, 368 ; *A.*, i, 152.

ready for plant growth. These observations are of great interest in connexion with the reclamation of alkali land.

The effect of calcium and of magnesium carbonates on the soil bacteria has been studied in some detail.[38] Both carbonates increase the numbers of *Azotobacter* and also of bacteria growing on gelatin plates, especially in acid soils; magnesium carbonate is more potent than calcium carbonate. The effect is in the main a neutralisation of acidity, but it is something more, because it increased by further additions after the neutralisation point is reached.

It has frequently been assumed that bacteriotoxins must exist in the soil, since they are known to be formed in certain culture media. The question has been examined very thoroughly, but all the supposed proofs are shown to be faulty.[39] The essential difference between an artificial medium and a soil is that in the former the bacterial flora is pure, or at any rate limited in variety, whilst in the soil it is exceedingly complex, many of the organisms depending on the products of activity of others. Not only could no experimental evidence of the existence of bacteriotoxins be obtained, but it was further shown that the assumption of toxins leads to difficulties. Thus, it is necessary to suppose that heating fresh soil for fifteen minutes is sufficient to produce toxins but not to destroy them, whilst heating for sixty minutes both produces and destroys them, and in the case of air-dried soils fifteen minutes' heat causes their decomposition.

Aeration and water supply of the soil are highly important factors in its relation to plant growth. Aeration has received particular attention in India under Howard and his co-workers. The effect of adding potsherds or sand to the Pusa soil is shown to increase nitrification[40] and plant growth; in the case of Java indigo, the increase was as much as 40 per cent. The effect is no doubt complex, but evidence is adduced to show that excess of carbon dioxide in soil air adversely affects plant development. Some highly important practical consequences follow. Flood irrigation on fine alluvial soils interferes with their ventilation by rapidly destroying the texture and forming a compact surface crust impermeable to air. One limiting factor, water, is removed, but another, the need of aeration, is introduced. Thus over-irrigation

[38] H. L. Fulmer, *J. Agric. Res.*, 1918, **12**, 463; see also F. E. Bear, *Soil Sci.*, 1917, **4**, 433.

[39] H. B. Hutchinson and A. C. Thaysen, *J. Agric. Sci.*, 1918, **9**, 43.

[40] A. Howard and R. S. Hole, *Indian Science Congress, Lahore*, 1918. *Indian Forester*, 1918, 187 : J. N. Sen, *J. Agric. Sci.*, 1918, **9**, 32. For the effect of oxygen and carbon dioxide on nitrification and ammonification, see J. K. Plummer, *Cornell Univ. Agr. Expt. Stat.*, 1916, *Bull.* 384 ; *A.*, i, 90.

actually diminishes the yield. This is further shown by results obtained at Quetta, where 13 maunds of wheat were obtained with one irrigation and only 8 maunds where three irrigations were given. In any flood irrigation system, therefore, a practical compromise between the needs of the plant for air and for water must be worked out. This has been accomplished at Quetta by the proper utilisation of the preliminary watering given before sowing. Under this new system, the yields obtained are often higher than with the six or seven waterings usually applied. The Quetta results have been shown by experiment to apply to the Punjab and Sind, where about half the irrigation water now used could be saved. The economic significance of these results becomes apparent when it is remembered that the annual revenue derived from irrigation works in India is £5,000,000 sterling.

It is further shown that aeration probably influences the distribution of plants, and is therefore of importance in ecological [40a] studies.

Finally, a new method of pot culture is described which allows close study of root development.[41]

The power of retaining water is intimately bound up with the size of the soil particles as revealed by mechanical analysis, and is especially marked in the case of the smaller particles. Thus, the "moisture equivalents"[42] of the separate fractions of a soil were as follows:[43]

Coarse fractions, down to and including the fine sand 0·10 mm. in diameter	1—2
Very fine sand (0·10 to 0·05 mm. in diameter) ...	4·6
Silt (0·05 to 0·005 mm. in diameter)	25
Clay (below 0·005 mm. in diameter)	61

The equivalent for the whole soil, however, is not the sum of the equivalents of the separate fractions, although it is not greatly different, but soils of the same mechanical analyses did not have the same equivalents. Methods of calculating equivalents are based on the assumption that the property is additive, and therefore not wholly trustworthy. The moisture equivalent is affected by salts, especially after they have been washed out; it is assumed that

[40a] For the benefit of chemists who are out of touch with modern botany it may be said that ecology deals with the relationships between the plant and its environment.

[41] A. Howard and G. L. C. Howard, *Agric. J. India*, 1918, 36.

[42] For methods of determination, see F. J. Alway, M. A. Kline, and G. R. McDole, *J. Agric. Res.*, 1917, **11**, 147; *A.*, ii, 47.

[43] A. Smith, *Soil Sci.*, 1917, **4**, 471.

this results from changes in the degree of dispersion of the soil particles, and the consequent alteration in the interfacial surface.[44]

The relationship of physical texture of soil to crop production in India has also been discussed.[45]

Fertilisers.

Work on fertilisers has been confined in the main to methods of increasing supplies, on which serious inroads were made by the Ministry of Munitions. The problems were of considerable technical interest, but no new scientific principle was brought out; an account is given in the Report to the Society of Chemical Industry, and need not be repeated here.

Perhaps the most important scientific work was on cyanamide. For long it has been known that this substance under certain conditions changes to dicyanodiamide;[46] the agricultural interest in the change lies in the fact that dicyanodiamide is toxic to plants, whilst cyanamide is a valuable fertiliser. It is now shown [47] that dicyanodiamide is also toxic to the nitrifying organisms, but it does not stop ammonia production; in admixture with cyanamide it scarcely impeded the production of ammonia, but completely prevented the further changes to nitrate. There are considerable differences between ammonia and nitrate as plant nutrients, the former being, on the whole, less efficient than the latter. No evidence could be adduced that dicyanodiamide breaks down in the soil, although cyanamide easily decomposes; whatever the reaction may be, it clearly cannot involve the formation of dicyanodiamide.

Plant Growth.

The most fundamental process in plant growth is the assimilation of carbon dioxide and its transformation into sugar. The physical processes were elucidated in 1900 by H. T. Brown and F. Escombe in à classical series of investigations, which was again presented with great advantage to the younger chemists by Dr. Brown in his lecture before the Chemical Society in May.[48] The

[44] L. T. Sharp and D. D. Waynick, *Soil Sci.*, 1917, 4.

[45] D. Clouston and A. R. P. Aiyer, *Agric. J. India*, 1918, 89.

[46] A paper on the constitution of dicyanodiamide deserves mention W. J. Hale and F. C. Vibrans, *J. Amer. Chem. Soc.*, 1918, **40**, 1046 ; *A.*, i, 380. The authors favour the cyanoguanidine structure, $NH_2 \cdot C(:NH) \cdot NH \cdot CN$, suggested by Bamberger in 1880.

[47] G. A. Cowie, *J. Agric. Sci.*, 1918, **9**, 113: confirmed also by L. Moller, *Biochem. Zeitsch.*, 1918, **88**, 85 ; *A.*, i, 469.   [48] *T.*, 1918, **113**, 559.

chemical processes are not clearly worked out. Baeyer's well-known hypothesis that formaldehyde is the first product has met with considerable criticism, but has recently been strongly supported in Germany. It is pointed out [49] that of all possible primary products, formaldehyde is the only one in the formation of which the volume of carbon dioxide absorbed is equal to that of the oxygen liberated. The so-called "assimilatory quotient" CO_2/O_2, which is therefore 1 in the case of formaldehyde, is 1·33 for glycollic acid, 2 for formic acid, and 4 for oxalic acid. Now precise determinations show that the quotient is exactly 1 whether the temperature is 10° or 35°, whether the atmosphere is rich in carbon dioxide or even free of oxygen altogether, and whether ordinary foliage or xerophytic leaves like cactus are examined.

In spite of this kind of negative evidence many chemists remain unconvinced, an important difficulty being that carbon dioxide cannot by any known process be reduced to formaldehyde, and even its reduction to formic acid is only brought about by powerful agents which in no wise reproduce the conditions in the plant. To some extent the difficulty is diminished by the discovery [50] of a new reaction whereby the reduction of carbonic acid to formic acid occurs with the intervention only of hydrogen peroxide, which is known to occur regularly in plants. When a saturated solution of potassium hydrogen carbonate reacts with a 10 per cent. solution of hydrogen peroxide, the following change takes place:

$$H_2O_2 + \frac{H}{K}\begin{bmatrix}O\\O\end{bmatrix}>CO = H_2O + O_2 + H \cdot CO_2 K.$$
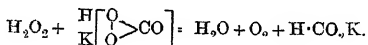
So far as it goes this is helpful, but there still remains the further reduction to formaldehyde, which, the author admits, is altogether a more difficult step.

The formaldehyde is then supposed to change to sugar, which is temporarily stored as starch, but sooner or later passes from the leaf to the storage organ, whether grain, stems, root, or tuber, in which it is stored in some characteristic manner. Some plants, such as Jerusalem artichoke, dahlia, and chicory, store the carbohydrates as inulin in their roots. Direct experiment with these has shown [51] that the inulin is certainly not found in the leaf or translocated as such; it occurs only in the underground organ, being formed from sugars translocated from the leaf.

[49] R. Willstätter and A. Stoll, *Ber.*, 1917, **50**, 1777; *A.*, i, 207. For a method of measuring photosynthesis see W. J. V. Osterhout, *Amer. J. Bot.*, 1918, **5**, 105, and *Science*, 1918, **47**, 420; *A.*, i, 471.

[50] H. Wislicenus, *Ber.*, 1918, **51**, 942; *A.*, i, 473.

[51] H. Colin, *Compt. rend.*, 1918, **166**, 224; *A.*, i, 151.

During the period of rest, however (that is, during the winter months), the inulin becomes gradually converted into sucrose and lævulosans.[52]

An investigation has been made of the carbohydrates of mulberry leaves which, apart from its physiological interest, has a practical bearing in that it deals with the food of the silkworm.[53]

The nitrogen required by the plant is taken up in the form of nitrate, but it obviously has to undergo important changes before it appears in the final form of protein; in particular, there must be a reduction either of the nitrate or of a nitro-compound. It has been shown[54] that ferrous sulphate and sodium carbonate react with aldoses, ketoses, catechol, quinol, quercetin (representing yellow plant pigments), chrysarobin (representing the anthranols), and other plant constituents to form a complex compound which in the presence of oxygen can carry out either reduction, converting nitrites to nitric oxide and ammonia, or nitrobenzene to aniline. Further, all these compounds are autoxidisable; they take up oxygen, and in presence of water produce hydrogen peroxide.

The iron exists as an "internal complex" and does not show the ordinary reactions; only traces are needed, but its presence is essential; neither manganese nor copper has the same effect.

It is particularly interesting that these widely distributed organic substances should have the power of bringing about oxidations on the one hand, and, in the presence of iron, reductions on the other, and that both reactions should take place in the presence of oxygen.

Numerous investigations have been made of other organic constituents of plants. One by Everest, on the production of anthocyanins and anthocyanidins[55] in plants, is of interest because for the first time it shows the presence in the same flower of an anthocyanin pigment and of the flavonol derivatives from which it would be formed by reduction. The anthocyanin pigment of the purplish-black viola "Black Knight" is shown to be a delphinidin glucoside identical with the violanin obtained by R. Willstätter and F. J. Weil.[56] The yellow sap pigment from the same pansy contains a myricetin glucoside and another yellow sap pigment which does not give a green coloration with dilute alkalis.

The pigment of myrtle berries has been examined, and is said to be identical with œnocyanin, the colouring matter of wine.[57]

[52] H. Colin, *Compt rend.*, 1918, **166**, 305 ; *A.*, i, 208.

[53] S. Kawase, *J. Tokyo Chem. Soc.*, 1918, **39**, 245 ; *A.*, i, 476.

[54] O. Baudisch, *Ber.*, 1918, **51**, 793 ; *A.*, i, 474.

[55] A. E. Everest, *Proc. Roy. Soc.*, 1918, [B], **90**, 251 ; *A.*, i, 420.

[56] R. Willstätter, and F. J. Weil, *Annalen*, 1916, **412**, 178 ; *A.*, 1917, i, 46.

[57] C. Marini, *Annali Chim. Appl.*, 1918, **10**, 32 ; *A.*, i, 519.

The occurrence of carotin in various seeds has been recorded; it was found in the seed of flax, mustard, and black sesame, but not in the seed of rape, white sunflower, turnip, safflower, or cotton.[58]

Great possibilities are suggested by a research started in America[59] to discover the substances in the cotton plant which prove so attractive to the boll weevil. This insect causes disastrous losses, and there is no certain means of control. If the attractive substance could be discovered it might be used for baiting traps, and if, better still, it could be bred out of the plant, much might be accomplished.

The phytosterols of wheat have received some attention; it is shown[60] that sitosterol is the chief representative of this group in the wheat grain, although another occurs in the bran. The quantity present in the young plants is greater than that in the original grain so long as growth is normal, but in etiolated plants there is a falling off. It is suggested that these sterols form an essential part of the cell membrane. Representatives of the group are also found[61] in the lower plants—fungi, seaweed, sphagnum, agaricus, etc.

Of the nitrogen compounds in plants, the legumin in peas has been shown to consist of at least two distinct substances, one soluble and the other insoluble in dilute salt solution, but the latter is extractable by water or dilute alkali and can be precipitated with dilute acetic acid.[62]

The protein of the Chinese velvet bean has been shown to consist mainly of a new globulin, to which the name stizolobin is given; [63] examinations have also been made of the globulin of buckwheat[64] and the stachydrin of lucerne.[65]

An improved method has been devised[66] for extracting nucleic acid from yeast and from wheat embryos; the purified products were found to contain nitrogen and phosphorus in the proportions required by Levene's[67] formula, $C_{38}H_{50}O_{29}N_{15}P_4$.

The complex carbohydrates, cellulose, pectins, furfuroids, etc,

[58] A. H. Gill, *J. Ind. Eng. Chem.*, 1918, **10**, 612 ; *A.*, i, 476.

[59] A. Viehoever, L. H. Chernoff, and C. O. Johns, *J. Agric. Res.*, 1918, **13**, 345 : see also E. E. Stanford and A. Viehoever, *ibid.*, 419.

[60] M. T. Ellis, *Biochem. J.*, 1918, **12**, 160 ; *A.*, i, 420.

[61] *Ibid.*, **12**, 173 ; *A.*, i, 420.

[62] O. Hammarsten, *Zeitsch. physiol. Chem.*, 1918, **102**, 85 : A., i, 509.

[63] C. O. Johns and A. J. Finks, *J. Biol. Chem.*, 1918, **34**, 429 ; *A.*, i, 316.

[64] C. O. Johns and L. H. Chernoff, *ibid.*, 439 ; *A.*, i, 315.

[65] H. Steenbock, *ibid.*, 1918, **35**, 1 ; *A.*, i, 476.

[66] G. Clarke and S. B. Schryver, *Biochem. J.*, 1917, **11**, 319 ; *A.*, i, 130.

[67] P. A. Levene, *Biochem. Zeitsch.*, 1909, **17**, 120 ; *A.*, 1909, i, 541.

form a large part of the plant tissue, but their chemical characterisation is still very incomplete, and no great additions to our knowledge can be recorded this year.

Recent investigation has brought out the fact that cellulose is not hydrolysed to dextrose, as was formerly supposed, but to more complex esters of polysaccharides which contain acidic hydroxyl groups.[68] The constitution suggested for cellulose, which supposes it to be a polydextrose anhydride, is therefore without experimental support. More definite evidence has been put forward of the occurrence of methyl pentosans in cereals and the soya bean,[69] on which doubts have been cast, and it has again been emphasised that other substances besides pentoses and pentosans yield furfuraldehyde under the conventional method of distillation with hydrochloric acid.[70]

Investigation of the pectins, the basis of fruit jellies, has brought out little more than the facts that methyl alcohol can be split off, and that various preparations yield furfuraldehyde corresponding with between 35 and 46 per cent. of arabinose and 6 and 10 per cent. of methyl pentose.[71]

The chief phosphorus compounds of wheat and other cereal grains are orthophosphoric acid and inositolpentaphosphoric acid, $C_6H_6(OH)(H_2PO_4)_5$.[72]

Many attempts have been made to ascertain the functions of the numerous organic substances found in plants, or, less ambitiously, to discover whether they are harmful or beneficial to the plant. Many are harmful, especially in water culture, but in at least one case[73] the plant is immune to the toxic principle it itself produces; *Agrostemma githago* is not affected by its glucoside agrostemma-saponin even in 1 per cent. solution, whilst peas, radishes, and buckwheat are markedly injured by as little as 0·01 per cent. Other compounds are somewhat specific in their effects. Mandelonitrile almost prevents germination, but is not poisonous afterwards, although when given to seedlings it so alters the habit of growth as to give the appearance of a new species; strychnine, morphine, and caffeine, on the other hand, do not prevent germination, but are toxic afterwards.

Some of the results suggest that the alkaloids may have a definite

[68] M. Cunningham, *T.*, 1918, **113**, 173.

[69] K. Oshima and K. Kondō, *J. Tokyo Chem. Soc.*, 1918, **39**, 185, 294; *A.*, i, 419; ii, 338.

[70] R. Gillet, *Bull. Assoc. Chim. Sucr.*, 1917, **35**, 53; *A.*, ii, 248.

[71] T. von Fellenberg, *Biochem. Zeitsch.*, 1918, **85**, 118; *A.*, i, 215.

[72] J. B. Rather, *J. Amer. Chem. Soc.*, 1918, **40**, 523; *A.*, i, 212.

[73] R. Combes, *Compt. rend.*, 1918, **167**, 275.

function in plants,[74] perhaps that of hormones. Just as in animals the adrenaline of the suprarenal glands is produced from tyrosine, so in plants the waste products, originally indifferent, may be transformed to something serviceable.

The curious observation is recorded that galactose and mannose even in dilute solutions are very toxic to the roots of peas and wheat, although dextrose and sucrose were able to act as antidotes.[75] Hydrocyanic acid is likewise extremely toxic, 1 part in 100,000 of the culture solution being sufficient to kill immediately; sodium cyanide proved equally toxic. Neither compound showed any sign of a stimulating effect in any dilution.[76]

Results obtained in water culture are of considerable physiological interest, but they do not necessarily show what happens in the soil, for it is well known that considerable biochemical transformations take place in soil, and organic compounds toxic in water may be decomposed quickly. Thus vanillin, whilst immediately harmful as in water culture, soon disappears[77] and leaves no after-effects.

The inorganic plant nutrients figure much more prominently in agricultural chemistry than the organic constituents of the plant, because they are more under control. The process by which they are absorbed is commonly considered to lie outside the purview of the agricultural chemist, but is of never-failing interest to the physiologist, and there is a constant flow of papers on its various aspects. Osterhout and his school regard the process as physical; Stiles and Jorgensen consider it to be chemical.[78]

One of the most remarkable of the phenomena connected with the inorganic plant nutrients is the injury caused to the plant when single substances, and not mixtures of substances, are presented to the roots, or when one substance greatly preponderates over others. A full investigation was made by Tottingham[79] four years ago; eighty-four different mixtures of four salts were used for plant growth; all had the same total concentration, but the proportions of the four ingredients varied; some of the solutions caused specific injury to wheat seedlings, whilst others produced excellent growth

[74] G. Ciamician and C. Ravenna, *Gazetta*, 1917, **47**, ii, 109; *Atti R. Accad. Lincei*, 1918, [v], **27**, i, 38; *A.*, i, 93, 473.

[75] L. Knudsen, *Amer. J. Bot.*, 1917, **4**, 430; *A.*, i, 95.

[76] Miss W. E. Brenchley, *Ann. Bot.*, 1917, **31**, 447; *A.*, i, 95.

[77] M. J. Funchess, *Alabama Agric. Expt. Stat. Bull.* 191, 1916; *A.*, i, 150.

[78] W. J. V Osterhout, *Bot. Gaz.*, 1917, **63**, 77, 317; *A.*, i, 472. S. C. Brooks, *ibid.*, 1917, **64**, 230, 306; *A.*, i, 472; W. Stiles and I. Jorgensen, *Ann. Bot.*, 1917, **31**, 415; *A.*, i, 94; *Bot. Gaz.*, 1918, **65**, 526; W. Stiles and F. Kidd, *Proc. Roy. Soc.*, 1918, **11**.

[79] *Physiol. Research*, 1914, **1**, 133.

and had no toxic effects. These observations have been considerably extended. Magnesium [80] and phosphoric acid in certain proportions both tend to produce injury, especially when the total concentration exceeds a certain point. Monocalcium phosphate in its toxic doses was more harmful than potassium phosphate, but the effects were quite definite.[81] Ammonium sulphate also causes injury when given alone or in preponderating quantity in a mixture. Where increased yields are obtained they are due, not to additional nitrogen, but to a redressing of a disturbed balance.[82] Indeed, the American physiologists consider that the cation of any single salt is toxic, but its toxicity is overcome in a properly balanced mixture of two or more salts. The French investigators claim an exception in calcium,[83] at any rate in its effects on seedling growth; for in the presence of a calcium salt seedling growth is much more rapid than in pure water, but this effect is decreased and not heightened by the addition of other salts. Thus the different metals, whether toxic or nutritive, are antagonistic to calcium in seedling growth, just as calcium is anti-toxic towards them. A close relationship is claimed [84] between antagonism and effects on permeability, all solutions which permit normal growth preserving normal permeability.

Investigation continues of the effect of other inorganic elements besides the classical three (nitrogen, phosphorus, and potassium); J. A. Voelcker in the Hills's experiments has examined magnesium salts; American investigators have found lithium in all plants examined, rubidium in most, and cæsium in a few,[85] whilst it is also shown [86] that aluminium occurs only in small quantities in xerophytes, but in much larger amounts in other plants. The effect of boron compounds on plant growth has been examined.[87]

There is little to record in the investigation of crop composition; quality of crop, once of interest to the agricultural chemist, has receded to the background in a hungry world clamouring only for quantity. One paper has appeared on the old problem of the

[80] For injurious effect of magnesium carbonate in water cultures, see H. Coupin, *Compt. rend.*, 1918, **166**, 1006; for soil experiments, see J. A. Voelcker, *J. Roy. Agric. Soc.*, 1916, **77**, 244.

[81] J. W. Shive, *Soil Sci.*, 1918, **5**, 87.   [82] M. I. Wolkoff, *ibid.*, 123.

[83] L. Maquenne and E. Demoussy, *Compt. rend.*, 1918, **166**, 89; *A.*, i, 149.

[84] W. J. V. Osterhout, *Science*, 1917, **45**, 97; *A.*, i, 471: see also L. W. H. van Oyen, *Biochem. Zeitsch.*, 1918, **87**, 418; *A.*, i, 472, who attempts to correlate the physical properties of the salts with their biological action.

[85] W. O. Robinson, L. A. Steinkoenig, and C. F. Miller, *U.S. Dept. Agr., Bull.*, 1917, No. 600; *A.*, i, 331.

[86] J. Stoklasa and others, *Biochem. Zeitsch.*, 1918, **88**, 292; *A.*, i, 475.

[87] F. C. Cook and J. B. Wilson, *J. Agric. Res.*, 1918, **13**, 451.

strength of wheat,[88] the main point of which is that the gluten of weak flour is a different chemical unit from the gluten of strong flour, coming nearer the boundary which separates the crystalloid from the colloid state.

The problems of grain storage have received attention,[89] and in crop growth more data have accumulated on the comparative rates of transpiration of maize and sorghum[90] and on the relationship of the density of cell sap to the ability of plants to survive low temperature.[91]

Feeding Stuffs.

The chief concern of agricultural chemists in this country has been to show how the limited supplies of feeding stuffs might be used to the best advantage, but in countries affected by the blockade there has been a vigorous search for substitutes for which much success was claimed. The best is said to have been straw digested with dilute sodium hydroxide solution, but a number of others—leaves, heather meal, etc.—have been used; they are described in the Report to the Society of Chemical Industry.

Of scientific work, perhaps the most interesting comes from State College, Pennsylvania. The low return for the last pound of food in fattening is traced to the increased maintenance requirement of the fat as compared with the lean ox; it is not due, as has commonly been supposed, to the falling off in efficiency of utilisation of the nett energy.[92] Dr. Armsby has summarised his researches in a new volume, "The Nutrition of Farm Animals," which will be welcomed by agricultural chemists. It may be noted that he attaches less importance than usual to starch equivalents, which, he considers, may obscure the energy relationships.

Several digestibility studies have been completed. The power of digesting starch is shown to increase rapidly in the young calf between the fourth day and the third week after birth.[93] In older animals, the digestion coefficients are said to be reduced when foods are given together instead of singly.[94]

The efficiency of various proteins for purposes of milk production has been determined, the protein of distillers' grains being

[88] R. A. Gortner and E. H. Doherty, *J. Agric. Res.*, 1918, **13**, 389.
[89] C. H. Bailey and A. M. Gurjar, *ibid.*, 1918, **12**, 685.
[90] S. C. Salmon and F. L. Fleming, *ibid.*, 1918, **13**, 497.
[91] E. C. Miller and W. B. Coffmann, *ibid.*, 1918, **13**, 579.
[92] H. P. Armsby and J. A. Fries, *ibid.*, .1917, **11**, 451 ; 1918, **13**, 43.
[93] R. H. Shaw, T. E. Woodward, and R. P. Norton, *ibid.*, 1918, **12**, 575.
[94] P. V. Ewing and F. H. Smith, *ibid.*, 1918, **13**, 611.

more effective than that of gluten feed. which again is more effective than that of cotton seed.[95]

Milk.

The composition of milk has received some attention. The very complex mixture of glycerides forming the fat has been again examined,[96] and a new method of esterification suggested, based on the use of hydrochloric acid as catalyst.[97]

A new protein has been found in milk resembling the gliadin of wheat in its solubility in 50—80 per cent. alcohol; several previously described proteins have been more definitely characterised.[98] The method of preparation of pure caseinogen from milk has been considerably improved.

A method for isolating citric acid from milk is described,[1] and the mechanism of the souring process discussed.[2]

Further data have been published on the old question as to the relationship between yield of milk and percentage of fat. A negative correlation was found; where the yield was high the fat was low, and vice versa.[3]

Fermentation.

Slator has continued his investigations on the phenomena of the growth of yeast, and shows that it involves three stages: a lag-phase or period of quiescence, during which there is no growth; a period of unrestricted growth, when the rate follows a logarithmic law; and a period of retardation, due to the accumulation of carbon dioxide or deficiency of oxygen.[4]

An important experimental confirmation has been obtained of the hypothesis that acetaldehyde is an intermediate product in the formation of alcohol by fermentation. Action can be stopped at this stage if the process is carried out in presence of sodium sulphite; the acetaldehyde then accumulates in the form of the

[95] E. B. Hart and G. C. Humphrey, *J. Biol. Chem.*, 1918, **35**, 367 ; *A.*, i, 465.

[96] C. Amberger, *Zeitsch. Nahr. Genussm.*, 1918, **35**, 313 ; *A.*, i, 418.

[97] E. B. Holland and J. P. Buckley, jun., *J. Agric. Res.*, 1918, **12**, 719 ; *A.*, ii, 250.

[98] T. B. Osborne and A. J. Wakeman, *J. Biol. Chem.*, 1918, **33**, 7 ; *A.*, i, 141.

[99] L. L. Van Slyke and J. C. Baker, *ibid.*, **35**, 127 ; *A.*, i 413.

[1] H. H. Sommer and E. B. Hart, *ibid.*, 313 ; *A.*, i, 465.

[2] L. L. Van Slyke and J. C. Baker, *ibid.*, 147 : *A.*, i, 417.

[3] E. Roberts, *J. Agric. Res.*, 1918, **14**, 67.

[4] A. Slator, *Biochem J*, 1918, **12**, 248 ; *A.*, i, 564.

bisulphite compound, no less than 73·5 per cent. of the theoretical quantity being obtained. Further, it is shown that acetaldehyde is readily reduced to ethyl alcohol during fermentation.

On the other hand, there has been severe criticism of Lebedev's hypothesis that the hexoses break down to trioses, which are then converted into alcohol and carbon dioxide.

The formation of hexosephosphoric acid was, of course, established by Harden and Young, but it is regarded by Neuberg as a pathological phenomenon and not as a true intermediate process in the living yeast cell.[5] In this investigation, the formula ascribed by Harden and Young to hexosephosphoric acid, $C_6H_{10}O_4(PO_4H_2)_2$, has been confirmed, and further properties are recorded. It cannot be fermented by living yeasts even in the presence of co-ferments or artificial activators, nor can its salts.

Further work has been done on the nature of the co-ferment. Examination has been made of the hypothesis that a mixture of ketonic acids and potassium phosphate acts as a co-ferment, and this has been confirmed;[6] here, however, the evidence is not regarded by Harden as sufficient. A large number of aldehydes accelerate fermentation.[7]

Two important papers have appeared on the enzymes concerned in the decomposition of dextrose and mannitol by *Bacillus coli communis*.[8] The view is taken that the fermentation of carbohydrates by bacteria is effected by a definite set of enzymes which act in the same way in all cases. A common intermediate substance is therefore assumed, the production of which may require special enzymes, but the subsequent stages are always similar.

In development of this view, it is shown that alcohol, acetic acid, and succinic acid are probably formed from the common intermediate substance by one reaction and lactic acid by another, each accelerated by specific enzymes.

Papers have appeared on yeast metabolism, which, however, are dealt with in the section on Physiological Chemistry.

A bacterial catalase has been described.[9]

E. J. RUSSELL.

[5] C. Neuberg and E. Reinfurth, *Biochem. Zeitsch.*, 1918, **89**, 365, ; *A.*, i. 317.

[6] C. Neuberg, A. Levite, E. Färber, and E. Schwenk, *ibid.*, 1917, **83**, 244 ; *A.*, i, 91.

[7] C. Neuberg, *ibid.*, 1918, **88**, 145 ; *A.*, i, 469.

[8] E. C. Grey, *Proc. Roy. Soc.*, 1918, [B], **90**, 75, 92 ; *A.*, i, 144.

[9] M. Jacoby, *Biochem. Zeitsch.*, 1918, **88**, 35 ; **89**, 350 ; *A.*, i, 469, 517.

RADIOACTIVITY.

THE Annual Report this year comprises the work done in 1917 and 1918, and is, as regards the work published in Germany and Austria, subject to limitations imposed by the censorship in these countries, although probably most of the investigations in this field are included. The most important advances are concerned with the discovery of the parent of actinium, which, in addition to adding an interesting, chemically new, element to those discovered by radioactive methods, completes probably the long sequence of changes suffered by the radio-elements; very comprehensive researches on the γ-rays of radium, which throw much fresh light on the peculiarities observed in the absorption of these radiations and on their wave-length; and a notable beginning in the application of the Rutherford-Bohr model nuclear atom to the whole of the elements, preserving the best features of the original Thomson electronic atom, from which new experimental inquiries may be expected to originate.

The Parent of Actinium.   Ekatantalum.

The most probable mode of origin of actinium as a branch product of the main uranium–radium series has already been fully discussed and illustrated by a diagram.[1] It was expected that uranium-Y, isotopic with uranium-X_1 and ionium in the thorium place in the periodic table, and simultaneously formed with one of them in the dual α-ray change of either uranium-I or uranium-II, would prove to be the first member of the actinium series. Uranium-Y gives a β-radiation, and therefore its unknown product must occupy the "ekatantalum" place in the periodic table, and be isotopic with uranium-X_2, or brevium, the very short-lived product of uranium-X_1 in a β-ray change. If this unknown product of uranium-Y underwent an α-ray change, the product must be actinium or an isotope, and, if the change were slow, it

[1] *Ann. Report*, 1913, 267.

H 2

would account for this member not having been previously observed; but in this case it must be present in weighable quantity in uranium minerals.

In one investigation,[2] the hypothetical element was sought for in pitchblende by subjecting it to a treatment which had been found to be effective in volatilising its isotope, uranium-X_2, from uranium-X_1. It was found, by distilling a preparation of uranium-X in a current of air and carbon tetrachloride vapour at an incipient red heat, that uranium-X_2 could readily be volatilised from uranium-X_1. On applying the method to about 500 grams of a very rich Indian pitchblende, small sublimates were obtained in which the known pre-emanation members could not be detected, but in which the post-emanation members, polonium, radium-E, and probably radium-D, were present. The growth of actinium in these preparations was tested for by means of the active deposit produced. At first, all the preparations were free from actinium and gave neither an emanation nor an active deposit. The first preparation, obtained during the first twenty hours of the sublimation process, remained free from actinium. The second preparation was obtained by a simple continuation of the process at the same temperature for a further period of ninety hours, and this, in the course of 1000 days, continuously produced a distinct quantity of actinium, unmistakably characterised by means of the active deposit. At the end of this period, the quantity of actinium present was at least twenty times as great as sufficed for detection. A third sublimate, obtained by a further treatment of the material for six hours at a much higher temperature, remained free from actinium. Confirmation was obtained by the growth of actinium in another preparation, derived, from the insoluble matter that had slowly deposited from a nitric acid solution of Joachimsthal pitchblende on long keeping, by the carbon tetrachloride sublimation. Moreover, certain old uranium-X preparations, separated from 50 kilograms of uranyl nitrate in 1909, in which a growth of actinium too minute to be conclusive had been recorded in 1913,[3] by 1917 were found to contain actinium in increased amount, minute, but beyond all doubt.

The attempt was made, on the admittedly uncertain assumption that the whole of the ekatantalum had been separated from the mineral and was contained in the second sublimate—since none was found in the first, and the third, prepared by raising the temperature considerably, also remained free from actinium—to obtain an estimate of the life-period of actinium. The case pre-

[2] F. Soddy and J. A. Cranston, *Proc. Roy. Soc.*, 1918, [A], **94**, 384; *A.*, ii, 211.   [3] F. Soddy, *Chem. News*, 1913, **107**, 97.

sents complete analogy to the method used by Rutherford and Bolt-wood to find the life-period of radium, by separating the whole of the ionium from a mineral and determining the rate of growth from it of radium, in terms of the equilibrium amount of radium initially present in the mineral.[4]   On the assumption that the whole of the parent has been separated. the method gives the period of the product. although nothing is known as to the period of the parent.   It was found that the amount of actinium formed in 2·5 years from the ekatantalum preparation was equal to the amount of actinium in one two-thousandth part of the original mineral used in the preparation.   This gives for the period of average life of actinium 5000 years.   It is the maximum possible value, to be reduced in proportion as the separation of the eka-tantalum from the mineral was incomplete.   The minimum period, on the other hand, is given by the incomplete and preliminary observation of Mme. Curie, that the β-activity of an old actinium preparation had decreased 10 per cent. in three years. from which a period of average life of the order of only thirty years is to be inferred.[5]

In an independent investigation, the parent of actinium has been separated from uranium minerals and given the name "proto-actinium."[6]   At the outset, these investigators state that they have confirmed Mme. Curie's estimate, that the period of actinium is of the order of thirty years, by observations on the decay of the radiation over a period of seven years, as well as for several more recently prepared specimens.   This, if correct, indicates that in the carbon tetrachloride distillation less than 1 per cent. of the contained ekatantalum was removed.   So that there is at present a real conflict of evidence as to the period of this element, which still, after so many years, remains the chief lacuna in our know-ledge in this field.   However, it is a step in the right direction definitely to have confined it between the limits of thirty and 5000 years.

In this investigation. the siliceous residues remaining undis-solved after treatment of pitchblende with nitric acid provided the raw material for the search for the parent of actinium.   A small quantity of a tantalum compound was added, and the material treated with hydrofluoric acid.   The filtrate, after evaporation with sulphuric acid to dryness, was digested with con-centrated nitric acid.   The part undissolved, containing the tan-talum, was examined first as regards its α-radiation.   It was found to be giving an α-radiation, which increased with lapse of time.

[4] Compare *Ann. Report*, 1916. 265.   [5] *Ann. Report*, 1911, 290
[6] O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1918, **19**, 208 ; *A.*, ii, 345

On the expectation that the initial rays were due to the parent of actinium, and that these would be of low range in comparison with those later produced, derived from the products of actinium, the radiation was also examined under conditions such that the rays of lower range were suppressed. The expectation was confirmed. Under these conditions, the longer range α-rays were absent initially, but rapidly developed and grew in strength with lapse of time. With larger quantities of material, prepared in the same way, the growth of actinium was definitely established by the appearance, and increase in amount with lapse of time, both of the short-lived actinium emanation and the characteristic active deposit.

A careful determination was made of the range of the α-rays initially given by the preparation. The value obtained, 3·314 cm. of air at $N.T.P.$, enables a rough estimate of the period of the new member to be determined by means of the Geiger-Nuttall relation. Unfortunately, the actinium series does not obey this relation nearly as closely as the other disintegration series, and there is a considerable difference in the constants, according as actinium-X or radioactinium is taken for the comparison. From the former, the range corresponds with 1700 years, and from the latter with 260,000 years, as the period of average life of proto-actinium.

It is clear from this evidence, however, that the period of eka-tantalum or protoactinium must be such as to cause the equilibrium quantity accumulating in uranium minerals to be of the same order as for radium. This quantity, relative to that of radium, is as the ratio of the periods multiplied by 8/92, the branching factor. Since the new element occupies a place to itself in the periodic table, save for the hopelessly short-lived uranium-X_2, or brevium, it should possess unique chemical character and spectrum. Its separation from uranium minerals in a pure state, in quantities that will allow its atomic weight and spectrum to be determined and its various compounds to be prepared and studied, may therefore be confidently anticipated. This, in turn, will allow the preparation of actinium, in a manner similar to the preparation of radiothorium from mesothorium, to be carried out, and will much simplify the elucidation of the problems with regard to the period, atomic weight, and spectrum of that element which remain to be settled.

There is no reason to doubt that ekatantalum is the product of uranium-Y, but this probably, as in the case of the production of uranium-II from uranium-X_2, can never be the subject of direct proof owing to the unfavourable relations of the periods. There

remains the doubt, however, as to whether uranium-Y is the product of uranium-I or uranium-II, although the latter is perhaps the more probable. This point can only be settled by the determination of the atomic weight of ekatantalum or actinium. The first alternative makes the atomic weights 234 and 230, and the second 230 and 226, respectively.

In this connexion, a third very interesting alternative suggestion has been made, namely, that actinium is derived from a third distinct isotope of uranium, of atomic weight 240, which does not belong to the uranium–radium family at all, but is a distinct primary radio-element, for which the name "actinouranium" is proposed.[7] In support of this view, it is pointed out that the latest determination of the atomic weight of uranium by Hönigschmid, 238·16, corresponds exactly with what it should be were it a mixture of 92 per cent. of an isotope of atomic weight 238, corresponding with that of radium. 226·0, and 8 per cent. of an isotope of atomic weight 240, corresponding with an atomic weight of actinium, 232. Also, the fact that in the graph of the Geiger-Nuttall relation the three series are not superimposed, but give parallel lines, the constants being the same for each series but different for the different series, is evidence that the actinium series is a distinct primary series. The obvious objection is that, so far as is yet known at least, the ratio of actinium to radium in uranium minerals is constant, and, for this to be the case, actinouranium must have the same period as uranium-I. This question, also, must await for its answer the determination of the atomic weight of either ekatantalum or actinium; but it may be noted that, but for the assumed difference in the atomic weight, no experimental decision would be possible. There is no method of distinguishing between a single substance disintegrating dually to give two products and a mixture of two isotopes in the proper proportion, each isotope having the same atomic weight and *the same period*, although, of course, it would be an extremely unlikely chance that the periods of the two components of such a mixture would be the same.

Except for the decision between these three alternatives, it may thus be considered fairly probable that the complicated disintegration sequences of the radio-elements are now completely unravelled. Adopting as the most probable alternative that uranium-Y is produced from uranium-II, these sequences are illustrated in the accompanying figure, taken from a recent lecture to the Chemical Society.[8] The figure is to be read at an angle of 45°; the number

[7] A. Piccard, *Arch. Sci. phys. nat.*, 1917, [iv], **44**, 161 : *A.*, ii, 6,

[8] F. Soddy, *T.*, 1919, **115**, 1,

above or below each symbol indicates the period of average life, a ? signifying that the period is indirectly estimated from the range
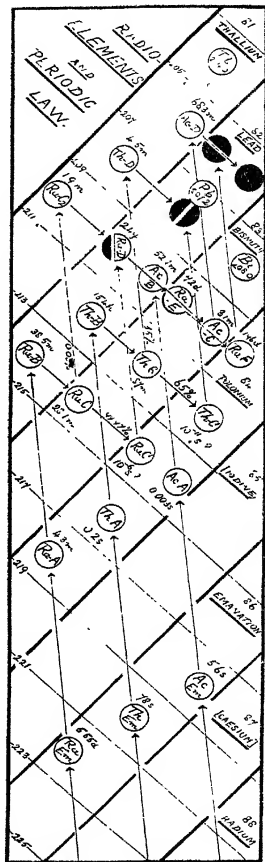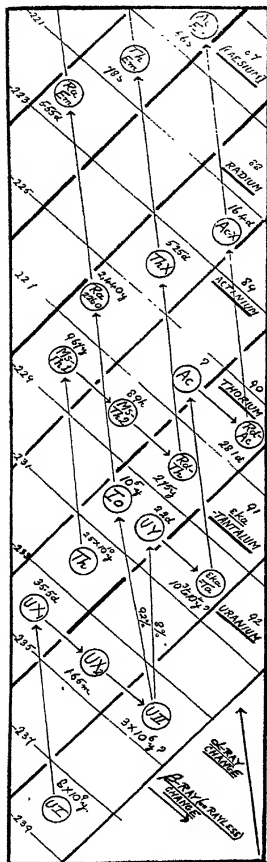
of the α-rays. The figures at the head of each place are the atomic numbers, as determined by Moseley from the wave-lengths of the

X-rays characteristic of the elements, on the assumption that that of aluminium, the thirteenth element in the list of known elements, is 13. It is to be noted that, should the stellar elements of Nicholson find places in the periodic table, these numbers will have to be increased. Of the twelve places between thallium and uranium covered by the disintegration series, two are vacant. The chemical and spectroscopic character of each of the individual members of the series is that of one of ten elements, of which five are common elements—uranium, thorium, bismuth, lead, and thallium—thoroughly well known before radioactivity was discovered, two are equally well known—radium and emanation—and only three, polonium, actinium, and ekatantalum, remain to be isolated in quantities sufficient for the spectrum and other properties to be determined. Apart from the great theoretical advances due to the explanation of the nature of radioactive change, the enormous simplification effected in the practical and technical problems connected with the preparation of the various members in the concentrated conditions from radioactive minerals must not be overlooked.

The Isotopes of Lead and Uranium.

In connexion with the determination of the atomic weights of lead derived from radioactive minerals,[9] one new atomic weight determination of thorio-lead has to be recorded.[10] This specimen of lead was prepared from a Norwegian thorite from Langesundfiord, and contained 30·1 per cent. of thorium, 0·45 per cent. of uranium, and 0·35 per cent. of lead. The Th/U ratio, 67, was thus somewhat higher than that, 57, for the lead from Ceylon thorite, which gave the value 207·77 for the atomic weight. The value in the present case was found by Hönigschmid to be $207\cdot90\pm0\cdot013$, and this is the highest value yet actually found for the atomic weight of this element.

In an attempt to obtain evidence as to whether common lead, with the atomic weight 207·2, is a single isotope or a mixture of the two derived from uranium and thorium, a comparison was made of the β-activities and the atomic weights of the contained lead from a number of uranium minerals of the same geological age.[10] The last-mentioned condition being satisfied, the β-activities, being derived from the lead isotope, radium-D, are a measure of the uranio-lead to total lead ratio for the mineral. This ratio will decrease, and the atomic weight of the lead increase, in pro-

[9] *Ann. Report*, 1916, 247, 272.
[10] K. Fajans, *Zeitsch. Elektrochem.*, 1918, 24, 163 ; *A.*, ii, 421.

portion as the lead separated from the mineral has not been produced from uranium, but is due to admixture. For three specimens of lead, derived from Joachimsthal pitchblende, the values found for the atomic weights, 206·405, 206·61, 206·73, and for the β-activities, in the ratio 1 : 0·639 : 0·55, were such as are to be expected if the lead were a mixture of uranio-lead and common lead of constant atomic weight 207·2. The question, however, whether ordinary lead is a definite single isotope or a mixture of isotopes of different atomic weights is likely to prove a difficult one. The constancy of the atomic weight of ordinary lead, as obtained from all sources, except the radioactive minerals, and even the proof that in the latter case the lead was a mixture of that derived from the radio-elements with ordinary lead of this constant atomic weight, although valid enough evidence pointing to the homogeneity of common lead, does not entirely settle the question, for it is possible to conceive of evolutionary processes in which different isotopes of the same element result necessarily in constant definite proportions, so that the product would simulate a homogeneous element.

It was pointed out by A. Holmes that the age of the Ceylon thorite, from which lead of atomic weight 207·77 was obtained, as calculated from the Pb/Th ratio, namely, 130 million years, was very much lower than is to be expected. A Ceylon pitchblende from the same locality, which he regarded as likely to be of the same age and as one of the most suitable minerals from which to calculate the age, had a Pb/U ratio 0·064, which corresponds with the geological age, 512 million years. To account for this and for the general poverty of thorium minerals in lead, which was the reason for the original conclusion that lead could not possibly be the ultimate product of thorium, it has been suggested that only one of the two isotopes of lead derived from the thorium series is permanently stable. The branching of the thorium series, as can be seen from the figure, results in the production of two isobaric isotopes with atomic weight 208. Since different amounts of energy are evolved in the two branches, the two products are not identical, and are likely to have different stabilities. If we take the analogy of the radium series, the isotope formed in major proportion, namely, the one in the 65 per cent. branch, is analogous to radium-D, which is not permanently stable, but disintegrates further, and, after one α- and two β-ray changes, finally gives the ultimate product of atomic weight 206. Such further changes have not yet been detected in the case of thorium, though, now that they are foreshadowed, it should be easy to decide definitely whether or not they occur. An important point is that in 20 kilograms of this thorite neither bismuth nor mercury could be

detected. These are the two elements which would result from a single β- or α-ray change respectively. A successive α- and β-ray change would result in thallium being produced, which was present in the thorite in quite noticeable amount. An examination of the Tl/Th ratio of minerals, and of the radioactivity of thorio-lead, is thus called for, but the war has hitherto prevented the suggestion being put to the test.

Assuming that only the 35 per cent. isotope of lead is permanently stable, the calculated age of the mineral is 375 million years, which is much more in accordance with the geological evidence. A further point is that the atomic weight found for the lead, 207·77, is less than it should be if the lead is wholly of radioactive origin and if both isotopes survived, but agrees exactly with the calculated value if only the 35 per cent. isotope is stable and the true atomic weights of uranio- and thorio-lead are exact integers, 206 and 208 respectively.[11] On the other hand, the more recent determination of the atomic weight, 207·90, for the lead from Norwegian thorite is about 0·08 too high on these assumptions.

Solubility of Salts of Isotopes.—It is to be expected that the molecular solubility of the salts of different isotopes will be the same, and therefore that, for salts of isotopes of different atomic weight, the solubilities and the densities of the saturated solutions will be different. A first attempt to put this to the test was recorded last year.[12]

In a second investigation,[13] lead of atomic weight 206·42 was compared with ordinary lead, and the molal solubilities of the nitrates at 25° were compared by estimating the lead in the solutions gravimetrically to the highest possible degree of accuracy. The result established conclusively that the molal solubilities of the two salts were identical within the very small margin of experimental error, that of the common lead nitrate being 1·7993 and that of the uranio-lead nitrate being 1·7991 gram-molecules per litre. With regard to the actual weight of lead per 100 grams of water, the figures, 37·281 for common lead and 37·130 for uranio-lead, are in substantially the same ratio as the known atomic weights.

On the same two specimens of lead nitrate a careful comparison of the refractive indices of the solid crystals failed to reveal any difference. At 20°, the value of n_D for each was 1·7814.

[11] F. Soddy, Royal Institution Lecture, May 18th, 1917; *Nature*, 1917, **99**, 414, 433.   [12] *Ann. Report*, 1917, 2.

[13] T. W. Richards and W. C. Schumb, *J. Amer. Chem. Soc.*, 1918, **40**, 1403; *A.*, ii, 422.

Uranium-I and Uranium-II.—In this section an attempt to separate the isotopes of uranium by diffusion methods may conveniently be referred to. There is a difference of four units in the atomic weight of uranium-*I* and uranium-*II*, and a separation by fractional diffusion should theoretically be possible. The relative rates of diffusion may, however, be expected to differ as the square-roots of the relative molecular weights, and even although the molecules diffusing are anhydrous, the difference to be expected between the diffusion coefficients is less than one-half per cent., whereas if the molecules of the salt, as is quite possible, are heavily hydrated in solution, this small difference will be still further diminished. The new attempt, like earlier ones, failed to effect any separation. Only an abstract of the work is available, in which it is stated that the experiment showed that the difference in the diffusion coefficients could not exceed 1·5 per cent. The case is, however, one of the most favourable for examination, because an alteration in the relative concentration of the two isotopes will cause a difference in the α-radiation of the uranium.[14]

Spectra of Lead Isotopes.—Previous work has shown that the spectra of isotopes, both the ordinary light spectra and the high-frequency or *X*-ray spectra, are identical within the limits of detection. As regards the high-frequency spectrum, this has been confirmed in a new instance to a very high degree of approximation. The two strongest lines in the *L*-series of lead, the so-called α- and β-lines, were photographed on the same plate and under the same conditions for two specimens of lead, one of atomic weight 206·05, from Morogoro uraninite, consisting essentially of uranio-lead, and the other, ordinary lead. The wave-length of the lines was found to be identical, within the error of measurement, which was estimated as 0·0001 Å.[15]

On the other hand, for ordinary lead and lead of atomic weight 206·34, estimated to contain one part of common lead to three parts of uranio-lead, the identity of wave-length of the strongest line in the light spectrum, of wave-length 4058, has been tested to a greater degree of approximation probably than has before been attained. This line was photographed with a 10-inch plane Michelson grating in the sixth order, under conditions such that a single Ångström unit corresponded with a distance of nearly 3 mm. on the photographic plate. The source of illumination was the Wali-Mohamed oxy-cathode arc in a vacuum, and, during the

[14] H. Lachs, M. Nadratowska, and L. Wertenstein, *Compt. rend. Soc. Sci. Warsaw*, 1917, **9**, 670; *A.*, ii, 213.

[15] M. Siegbahn and W. Stenström, *Compt. rend.*, 1917, **165**, 428; *A.*, 1917, ii, 524.

preliminary work, it was found that differences in the pressure caused differences in the intensities of the lines analogous to that noticed by Soddy for the line 4760·1 in his original comparison of the spectra of ordinary and thorio-lead. In the actual determinations, the two lamps containing the two specimens of lead were frequently interchanged in position. In every case, a minute difference in the wave-length of the line in question was observed, amounting in the mean to 0·0043 Å., the line in the case of uranio-lead having the longer wave-length, as is to be anticipated theoretically. A remarkable feature of the experiment was that the line in question was shifted, not broadened. Since the uranio-lead employed was certainly a mixture with common lead, this result is somewhat unexpected. As the authors themselves remark, it is well to await the result of entirely independent confirmation before concluding that the very minute difference in wave-length observed is due to the difference in atomic weight of the two specimens.[16]

Genesis, Nature, and Relations between the Chemical Elements.

A number of comprehensive accounts of the recent advances, often accompanied by attempts, more or less ambitious and indefinite, to interpret the constitution of the atom and the inter-relationship of the elements, have appeared, but these can only be briefly mentioned. The most promising direction of advance seems to lie in the direction of the interpretation of the light and high-frequency spectra, and the modification of the Rutherford-Bohr atom to bring it into line with the facts, as regards the elements other than hydrogen and helium, to which its initial successes were confined. This can most conveniently be dealt with in a separate section.

The attempt has been made to construct a model atom which shall explain in particular the chemical character of the elements.[17] The orbits of the outer valency electrons are regarded as being in general elliptical rather than circular. At the position of aphelion with regard to the nucleus, they will be travelling more slowly, and so be less resistant to forces tending to remove them from the atom. Those elements with variable valency are considered to have more elliptical orbits than those with constant valency, whilst for the argon gases the orbits are considered

[16] W. D. Harkins and L. Aronberg, *Proc. Nat. Acad. Sci.*, 1917, **3**, 710: *A.*, ii, 89; Compare T. R. Merton, *Proc. Roy. Soc.*, 1915, [A], **91**, 198; *A.*, 1915, ii, 119; *Ann. Report*, 1916, 248.

[17] A. W. Stewart, *Phil. Mag.*, 1918, [vi], **36**, 326; *A.*, ii, 395.

circular. Following the work of Fleck, who showed that quadri-
valent uranium has great chemical resemblance to thorium, not
amounting to the complete identity displayed by isotopes, an
analogy is drawn between the valency changes of an element, for
example, between ferrous and ferric iron, and the successive pro-
ducts of β-ray changes, in which the electron is withdrawn from
the nucleus rather than from the external ring of electrons. For
these successive products of β-ray changes, possessing essentially
the same atomic weight but different atomic number and distinct
chemical character, the term *isobares* is used.

In another paper, pointing out general relationships among the
radio-elements, another type of model atom is advocated, and the
connection between the structure, chemical linking, valency, and
electrochemical character discussed.[18] Lastly, another discussion
of the periodic law and the probable genesis of the elements, deal-
ing particularly with the accommodation of hydrogen, the rare
earths, and the stellar elements of Nicholson in the table, and the
new views introduced by the study of radioactive change, may be
mentioned. In this paper is contained a complete and independent
system of nomenclature of the radio-elements, on a definite and
consistent basis.[19]

X-Ray Spectra and the Constitution of the Atom.[20]

Bohr's theory, applied to the nuclear atom of Rutherford, ex-
plained the complete series spectrum of hydrogen and one of the
spectra of helium emitted when a single electron recombined with
the isolated nucleus. It also explained the nature and significance
of R, the universal frequency constant of Rydberg, and enabled
this to be calculated in terms of other fundamental constants to a
very high degree of approximation; but it did not give any
theoretical interpretation of series spectra in general, and hitherto
little attempt has been made to give any conception of the detailed
constitution of the elements as a whole. It was based on the two
fundamental assumptions (1) that in the normal state the electrons
were arranged in rings round the nucleus such that each electron
had angular momentum $m\omega a^2$ equal to $h/2\pi$, where m is the mass,
ω the angular velocity of the electron, h is Planck's constant, and
a is the radius of the orbit; (2) that the line of a series was pro-

[18] E. Kohlwoiler, *Zeitsch. physikal. Chem.*, 1918, **92**, 685; **93**. 1; *A.*,
ii, 286, 364.

[19] C. Schmidt, *Zeitsch. anorg. Chem.*, 1918, **103**, 79; *A.*, ii, 305.

[20] L. Vegard. *Phil. Mag.*, 1918, [vi], **35**, 293; *A.*, ii, 144; *Ber. Deut.
d. Ges.*, 1917, **9**, 328, 344; *A.*, ii, 93, 94.

duced, after the removal in some way of an electron from one of the rings, by its recombination in steps towards the broken ring between successive stability orbits, so that in one step one quantum of energy, $h\nu$, where ν is the frequency, was radiated. Much mathematical work has since been done in generalising the theory and applying it to non-circular orbits by Bohr, Sommerfeld, Schwarzchild, and Epstein.

The great extension of our knowledge of the high-frequency spectra of the various elements provides a further means of testing and extending the theory. One of the first generalisations, made by Kossel in 1914, was that the difference of frequency in the α- and β-lines of the K-spectrum of an element was equal, very approximately, to the frequency of the α-line of the L-spectrum. This was interpreted by Bohr to mean that the α-line of the K-spectrum was produced, after the removal of an electron from the ring next the nucleus, by its replacement by an electron from the second ring, the β-line by its replacement by an electron from the third ring, and the α-line of the L-spectrum by the replacement of an electron in the second ring by one from the third.

Recently, Debye,[21] as the result of an analysis based on certain fundamental assumptions, has succeeded in proving that the innermost ring of electrons, from which the K-series originates, consists of three electrons in the case of the elements between sodium and neodymium in the periodic table. For elements of higher atomic number than 30, the increasing mass of the electrons, due to their velocities increasing and becoming comparable with the speed of light, introduces difficulties into the exact calculation of the wavelengths of the radiations.

Vegard, making different alternative assumptions, although finally adopting the above conclusion as probably the one most likely to represent the constitution of the innermost ring, shows that the ring might be of four electrons, on the one further and physically perhaps improbable condition, that the K-radiation originated in all four electrons being removed together and recombining again as a unit to re-form the ring. He then proceeds to discuss the origin of the L-radiation, and shows that it is quite impossible to derive it by any recombination to a system in which the angular momentum of each electron is $h/2\pi$. One of Bohr's fundamental assumptions must be altered, and he assumes that the energy of the electron is in general $nh/2\pi$, where n is an integer having increasing value as we pass from ring to ring outwards from the nucleus, and to which he gives the name the quantnumber. It is only for the K-radiation and for the ring next the

[21] P. Debye, *Physikal. Zeitsch.*, 1917, **18**, 276; *A.*, 1917, ii, 434.

nucleus that the quant-number is unity and Bohr's original assumption applies.

As the result of his analysis and Debye's work, the K-series is to be attributed to a ring of three electrons nearest to the nucleus, for which the quant-number is unity. The L-series should be due to two rings, containing 7 and 8 electrons respectively, for which the quant-number is two, and the M-series to a ring of 9 or 10 electrons with the quant-number three. The new homogeneous J-radiation of Barkla and Miss White,[22] which is more penetrating even than the K-radiation, and is excited in aluminium by X-rays of wave-length 0·37 Å., he considers cannot be formed by any external electronic system, but must arise from electrons forming part of the nucleus. If this is so, it is clearly of fundamental importance, and, indeed, it is in this gradual sapping up to the nucleus of the atom as we pass from one external electronic ring to the other, and the hope it arouses that this may prove an avenue of approach to the problem of artificial transmutation, that the chief fascination in this field lies.

Taking as a very legitimate and probable view that in passing from the lighter to the heavier elements the system of electrons round the nucleus of the lighter element is preserved intact in the heavier and is gradually built round it, Vegard puts forward the following definite suggestions, combining the essential points of Sir J. J. Thomson's electronic atom with the conception of the nucleus. The elements from helium to fluorine have an internal ring of two electrons, the external system consisting of from 0 to 7 electrons, one being added for each element or for each step in atomic number. In all cases the nucleus changes, of course, with each change in the atomic number, the nett positive charge of the nucleus being equal to the atomic number, but the mass and constitution of the nucleus, which has no influence on the chemical character, are not further considered. At neon the added electron is transferred to the innermost ring, which, from now on, possesses three electrons; the outer ring of seven electrons is preserved intact as a new, complete second ring, from which the L-series originates. Since the K-series originates by transference of an electron from the second to the innermost ring, it should begin with the element sodium, a result in agreement with experiment. By continuing the process, at argon we have both L-rings with 7 and 8 electrons respectively, and the L-series of radiations may be expected to begin with the element potassium. In the long period from argon to krypton, a new ring of ten electrons is first completed by nickel, constituting the first M-ring with quant-number three. This is

[22] C. G. Barkla and Miss M. P. White, *Phil. Mag.*, 1918, [vi], **34**, 270.

followed by the formation of a new ring of eight electrons, and the process is repeated from krypton to xenon. The next four elements, from cæsium to cerium, are formed normally, the external valency system at the latter element comprising four electrons. From now it is supposed, to account for the rare earths, that this external system is kept intact, and the new electrons added go to produce a new inner ring, the members of which have a smaller quant-number than those outside. At the end of the rare earth elements this internal ring is completed, and the new electrons are added on as before.

The electrons forming the outermost system, which condition the ordinary chemical and electrochemical character of the element, are probably connected together as a whole in some unknown way, and in these phenomena act together as a unit rather than as individuals. Thus electro-affinity cannot be the measure of the energy required to remove one electron from the system, which is proportional to the ionising potential, a totally distinct quantity. The positive ray experiments of Sir J. J. Thomson have shown that the power of an atom to bind additional electrons does not follow the electro-affinity. The suggestion is put forward that the electro-affinity may be proportional to the energy required to remove an electron when all the other electrons of the system are simultaneously removed, which, according to Bohr, is equal to the kinetic energy of the electron. The mathematical analysis of this view leads to the expected results as regards the passage from electropositive to electronegative elements as the number of electrons in the outermost system increases, the elements with the more slowly moving electrons being the more electropositive, and also to the well-defined increase in the electropositive character with increase of atomic weight for elements of the same family. With regard to electric conductivity,[23] by means of the idea of atomic conductivity capacity, Benedicks has shown clearly that it must be regarded as a strictly periodic function of the atomic number. The atom is regarded as possessing an electric capacity C and to be in frictionless motion between two parallel planes, between which a certain potential is maintained. The electric conductivity due to the atom, K, is equal to the product of the capacity, C, and the frequency, or number of oscillations it executes per second, v. So the atomic conductive capacity is derived from the atomic conductivity, K, by dividing it by the atomic frequency, v. This quantity, plotted against the atomic number, gives a sharply periodic curve, in every respect analogous to that obtained when the atomic volume is plotted against atomic weight. Vegard con-

[23] C. Benedicks, *Jahrb. Radioaktiv. Elektronik.*, 1916, **13**, 362.

siders that the main features of this curve are to be expected on his view of the atomic structure, and that a great increase in electric conductivity is to be expected each time a new surface ring is commenced.

With regard to the nucleus of the atom itself, and the manner in which the contained electrons are disposed, the idea is put forward that for these the quant-number may be smaller than unity. There are difficulties in connexion with this view in that the velocities of the electrons would exceed that of light if the quant-number is made much less than unity. The γ-rays are much more penetrating than those of the K-series, and, like the new J-series already mentioned, must arise from the high-speed electrons within the nucleus. The line of shortest wave-length in the γ-ray spectrum of radium-C', with wave-length 0·072 Å., would be accounted for by assuming the electron to move within the nucleus between circles for which the quant-numbers are two-thirds and one-half, and the new J-radiation of aluminium by supposing the quant-numbers to be one-half and one-quarter. Without putting too much trust in the details of this theory of atomic structure, it presents us for the first time with a picture of the possible constitution of all the elements from one end of the periodic table to the other, which, however imperfect it may prove, is at least definite and capable of detailed quantitative examination and improvement as our knowledge of the high-frequency spectra of the elements grows.

The New J- and (?) I-Series of Characteristic X-Radiations.[24]— With regard to the new J-series of characteristic X-radiations, already referred to, these were put into evidence by determining the mass absorption coefficients in aluminium, paraffin wax, filter paper, and water of X-rays of wave-lengths between 0·51 and 0·145 Å., and then plotting these against those of copper, for which no J-radiation is expected to be excited by X-rays of this range of frequency. Discontinuities in the curves at wave-lengths 0·37 for water, due to oxygen, and 0·42 for filter paper, due to oxygen and carbon, the latter discontinuity being marked also for paraffin wax, and at 0·37 Å. for aluminium, revealed the existence of the new characteristic radiation, and the wave-lengths given correspond with these of the rays for carbon, oxygen, and aluminium, the effect of hydrogen in the compounds being negligible. These rays are a link between the K-series, the highest series of characteristic X-rays previously known, and the γ-rays of radioactive substances. It is just possible that a still higher series, an I-series of characteristic radiations, exists, but this has not yet been definitely shown.

[24] C. G. Barkla and Miss M. P. White, *Phil. Mag.,* 1918, [vi], **34,** 270.

Atomic Weight of Nebulium.[25]—By taking into account the magnetic as well as the electrostatic forces acting on the electrons in the atom postulated, the atomic weight of this element has been deduced, from the wave-lengths of the two principal lines in the spectrum, 5006·89 and 4363·37, to be 1·31, with a possible uncertainty of one unit in the last figure.

The γ-Rays of Radium.

From the newer point of view that the characteristic X-radiations of the various elements in the several series are due to the successive rings of electrons surrounding the nucleus, the wave-lengths of the radiations becoming the shorter and the rays the more penetrating the more nearly the nucleus is approached, the γ-rays appear to arise in a precisely analogous manner from rings of electrons contained within the nucleus. A clearer picture of their nature and origin is beginning to be formed.

In the first place, a very comprehensive and fruitful re-examination of the absorption of the γ-rays of radium by matter, and of the questions connected with their homogeneity and the "hardening" they undergo during the process of absorption, has been made with a very much larger quantity of radium—0·12 gram of radium chloride—than has before been available, which has greatly facilitated the clearing up of the points that the most careful work by private investigators with smaller resources left unsettled.[26] This work is to be interpreted in the light of the definition consistently adopted as to what is meant by absorption. Whether the energy of the beam is lost by conversion into heat, electronic or wave-radiation is regarded as irrelevant. The diminution of the energy over the area of the beam in its initial direction, whether by scattering, deflexion, or actual absorption, is regarded as absorption, as it is considered that only when scattered or secondary radiation is eliminated or corrected for can true absorption coefficients be obtained and the question of the complexity or homogeneity of the beam decided.

With the large quantity of radium, a narrow cone of γ-rays could be employed, which, after penetrating the absorbing plates, could

[25] J. W. Nicholson, *Month. Not. Roy. Astr. Soc.*, 1918, **78**, 349 ; *A.*, ii, 181 : compare *Ann. Report*, 1916, 256.

[26] K. W. F. Kohlrausch, *Jahrb. Radioaktiv. Elektronik.*, 1918, **15**, 64 ; also *Wiener Ber.*, *Mitt. Ra.-Inst.*, Nos. 97, 98, 99, 102 ; *Physikal Zeitsch.*, 1918, **19**, 345 ; *A.*, ii, 386. For accounts of the earlier work, compare *Ann. Report*, 1910, 268 ; 1911, 280 ; 1912, 296, 305 ; 1913, 281 ; 1914, 275 ; 1916, 262.

be passed through a magnetic field to eliminate electronic radiation, and the distance of the measuring instrument from the absorbing plates could be varied up to a metre if required. Many of the puzzling effects before encountered, when the cone had to be of wide angle and the screens close to the electroscope, at once became clear. Thus, when a plate of copper 0·4 cm. thick was introduced into the nearly parallel beam, and the distance of the ionisation vessel varied from 0 to 100 cm., the value of the absorption coefficient, μ, for copper varied from 0·284 to 0·522 (cm.$^{-1}$) as the contribution of the scattered and secondary γ-radiation from the absorbing plate to the ionisation decreased with the distance. In these circumstances, the "hardening" effect became constant after a thickness of 3·3 cm. of lead or its equivalent had been traversed. Thus, the absorption coefficients for the unscreened rays were 0·176 for aluminium, and this diminished to the constant value 0·125 when thicknesses of lead were introduced, no further change taking place after 3·3 cm. of lead. Similarly, the absorption coefficient for lead became constant after 3·3 cm. at 0·543. This value is higher than the most trustworthy value previously adopted, 0·500, owing to the difference in the conditions of measurement and the exclusion of the scattered and secondary radiation.

The absorption curve below the thickness of 3·3 cm. of lead was the sum of two exponential curves, the value of the coefficients being 0·543 for the more penetrating rays and 1·43 for the less penetrating rays. the ratio of the ionisations produced by the two radiations in the initial beam being as 1·3 : 1. For lighter metals, a third still softer radiation. absorbed in 3 mm. of lead, with the coefficient 4·6 in lead, was recognised. The general result of the analysis was to separate the γ-rays of radium into three homogeneous types of radiation, designated, in order of diminishing penetrating power, K_1, K_2, K_3, with ionisation energies in the ratio 8 : 6 : 1, and with absorption coefficients μ_1, μ_2, μ_3, as given for lead, 0·543, 1·43, 4·6, and for aluminium, 0·127, 0·230, 0·57 (cm.$^{-1}$). It will be observed that the ratio of the absorption coefficients is nearly twice as great for lead as for aluminium, which is a general feature of these very short waves.

Another point is that, so far as ionisation is concerned, the most penetrating radiation is the most powerful, and this no doubt explains to some extent the earlier conclusion that the rays were absorbed by lead, after the first centimetre, as a homogeneous radiation. The explanation of the definite conclusion of F. and W. M. Soddy, from experiments on the absorption in truncated hemispheres in a hemispherical ionisation chamber, capable of exact mathematical representation and investigation, that the radiation

was absorbed as a homogeneous beam, without scattering and production of secondary radiation, is not so clear, but is ascribed to a balancing of opposite effects. The heavy elements, which give rise to relatively little secondary radiation, absorb the less penetrating radiation the more strongly, whilst the lighter elements, which absorb the less penetrating radiation relatively less strongly, give rise to a strong secondary radiation. In the ordinary disposition, with absorbing plates close to an ordinary electroscope, the logarithmic absorption curve is, for light metals, slightly concave, and, for heavy metals, slightly convex to the origin.

As regards the values of the mass absorption coefficients, μ/ρ, where ρ is the density, for K_1 the extreme variation for different elements is only 15 per cent., the elements of mean atomic weight, as previously established, having the smaller values. Tin has the minimum value, about 0·04, which increases both for the lighter and the heavier elements. For K_2, the behaviour is more irregular, or perhaps to some extent a periodic function of the atomic weight. The value for the heaviest element, bismuth, 0·17, is about twice that for the lightest, aluminium, 0·085.

The full identification of these three types of γ-rays disclosed by the absorption phenomena with those disclosed by the crystal reflection method[27] is not yet possible. Using a linear relation of Siegbahn between the logarithm of the absorption coefficients in aluminium and the logarithm of the wave-length of the characteristic X-radiations of the various elements, and assuming what, according to the work of Barkla and Rutherford, is certainly not even approximately true, that this may be extrapolated into the region of very short waves, the values calculated for the wavelengths are: for K_1 0·139, for K_2 0·174, and for K_3 0·240 Å. K_3 is regarded as almost certainly the most penetrating type of γ-ray given by radium-B, and K_2 as the doublet, with wave-lengths 0·159 and 0·169, as measured by Rutherford and Andrade, of which one component was regarded as probably due to radium-B and one to radium-C. K_2, moreover, is considered as almost certainly the α-line of the K-series of the characteristic X-radiation of bismuth. K_1 does not, however, correspond with the most penetrating rays of wave-length 0·099 and 0·115 in the γ-ray spectrum of radium-C. In view of the recent conclusion of Ishino and Rutherford, still to be dealt with, that the penetrating γ-rays of radium-C are of very much shorter wave-length than any that have been resolved by crystal reflection, this whole attempt to correlate the results of the absorption and spectrum analyses must be regarded as doubtful.

[27] *Ann. Report,* 1913; 282; 1914, 276.

In another investigation, also with a large quantity of radium [28] and with a similar experimental disposition, the separate coefficients of scattering and absorption were determined for rays that had passed through 1 cm. of lead.   As regards the total emergent radiation, the rays are absorbed exponentially, and the observed coefficient is the sum of the true absorption and the scattering coefficients.   When the absorbing plate is at a sufficient distance from the electroscope, so that the amount of scattered radiation entering the electroscope may be considered negligible, the coefficient of the absorption curve is that of true absorption alone.   This neglects the increased absorption suffered by the scattered radiation in the plate, due to the thickness traversed increasing as the rays become oblique to their initial direction, but becomes the more nearly true as the absorbing plates decrease in thickness.   The experiments consisted in measuring the rays, confined to a narrow cone, with the absorbing plate in three positions : (1) near the source far removed from the electroscope; (2) close up to the front of the electroscope; (3) close up behind the electroscope, and extrapolating the values found for the scattering and absorption coefficients to zero thickness of absorber.   As the final result, the value of the scattering coefficient, σ, was taken to be 0·121 for aluminium, 0·334 for iron, and 0·397 for lead, the corresponding mass scattering coefficients, σ/ρ, being 0·045, 0·042, and 0·034 respectively. For μ and μ/ρ, the values in these three metals were, respectively, 0·070, 0·0263; 0·206, 0·0262; 0·460, 0·0423.   These results are of interest in two directions.   First, the scattering is very much less than for X-rays, for which it is practically independent of wavelength.   For example, Hull and Miss Rice, using the X-radiation of a Coolidge tube, found that the true mass absorption coefficient varied as the cube of the wave-length, but the mass scattering coefficient was 0·12, independent of the wave-length.   Since the total mass absorption coefficient found in these experiments with γ-rays, 0·076 for lead, was less than the scattering coefficient for X-rays, it is clear that the results of Hull and Miss Rice cannot be extrapolated to waves of shorter wave-length, and that for these the scattering coefficient decreases.   The second point is that the value of the total absorption coefficient in lead for the X-rays of wave-length 0·15 Å. is some forty times greater than for the hard γ-rays of radium, $(\mu+\sigma)/\rho$ being 3·00, as compared with 0·076. This makes it appear that the hard γ-rays of radium-C consist of waves very much shorter than any that have yet been observed by the crystal reflection method, the shortest wave-length so far observed being 0·071 Å.

[28] M. Ishino, *Phil. Mag.*, 1917, [vi], 33, 129.

These conclusions have been further developed by an examination of the X-rays from a Coolidge tube, generated by voltages between 79,000 and 196,000.[29] At the highest voltage, the absorption in lead could be followed over a range of 10 mm., but the intensity was cut down to less than one-millionth of the initial value by this thickness, although for the γ-rays of radium some twenty times this thickness would be necessary to produce practically complete absorption. Confining attention to the total mass absorption coefficients, $(\mu + \sigma)/\rho$, between the extremes of voltage mentioned, this changed from 2·37 to 0·75. From 105,000 to 144,000 volts, the rays were absorbed exponentially, and this coefficient remained constant at 1·93. At 183,000 volts it decreased from 2·28 to 1·05, as the thickness of lead increased from 0·7 to 7·0 mm. The homogeneous radiation obtained at intermediate voltage is undoubtedly due to the characteristic radiation of wavelength 0·149 Å., given by lead. After passing through screens of iron, the values of $(\mu + \sigma)/\rho$ in aluminium for the end radiation were 0·14, 0·11, and 0·085 for voltages of 92,000, 144,000, and 183,000 respectively.

The wave-length of the X-rays generated may be calculated closely from the voltage by the quantum relation $E = h\nu$, where E is the energy of the electron impressed on it by the voltage, h is Planck's constant, and ν is the frequency of the X-rays generated. These results showed that for high frequencies, the absorption coefficients, instead of varying at something like the cube of the wave-length, as in the case of X-rays of lower frequency, vary but slowly with the wave-length, and that the wave-lengths of the penetrating γ-rays of radium-C must be at least three times, and may be ten times, shorter than the shortest revealed by the crystal reflection method. Using the quantum relation, the observed radium-C γ-rays of wave-lengths 0·072 and 0·099 Å. correspond with a voltage of 174,000 and 125,000 volts. The values of $(\mu + \sigma)/\rho$ for X-rays excited at these voltages is 0·09 and 0·12. The main γ-rays of radium-C must correspond with X-rays excited at between 600,000 and 2,000,000 volts, and their wave-length must lie between 0·02 and 0·007 Å., which is about a hundred times less than the wave-lengths of the soft γ-rays of radium-B.

An examination of the voltage necessary to give the electron kinetic energy equal to that possessed by the various groups of β-rays in the magnetic spectrum of radium-B and -C[30] bears out this conclusion. Of the three types of γ-rays given by radium-B,

[29] Sir E. Rutherford, *Phil. Mag.*, 1917, [vi], **34**, 153 ; compare also Silvanus P. Thompson Memorial Lecture, *J. Röntgen Soc.*, 1918, **14**, 75.

[30] *Ann. Report*, 1911, 278.

the softest, $\mu = 45$ (cm.$^{-1}$), in lead, corresponds with a voltage of 200,000, and there are three strong groups in the β-ray spectrum of radium-B, the energies of which correspond with an average voltage of 200,000. The most penetrating type, which is also present in the γ-rays of radium-C, $\mu = 1·5$ in lead, corresponds with a voltage of 500,000, and β-rays with energies appropriate to this voltage are well marked in the β-ray magnetic spectra of both radium-B and -C.

Attempts to detect rays of shorter wave-length than those known in the γ-rays of radium-C by the crystal reflection method have failed. Possibly the crystal is unable to resolve waves so small in comparison with the grating-space. Rutherford now regards it as more probable that the transformation between β- and γ-rays occurs by single quanta rather than by multiple quanta, and that the multiple relations observed between the energies of some groups of β-rays must indicate approximate multiple relations between the frequencies of the γ-rays. Assuming that the single quantum relation holds, the magnetic spectrum of the β-rays should afford trustworthy data for extending the investigation of the X- or γ-ray spectra into the region of very short wave-length, where the crystal reflection method fails. If so, the extreme complexity of the magnetic spectra of the β-rays indicates that the spectrum of the γ-rays, and presumably the high-frequency spectra of heavy elements in general, are in reality just as complex as their ordinary light spectra.

The Active Deposits.

An investigation of the effect of different atmospheres on the distribution of the active deposit in an electric field has shown that the final condition of the particle, recoiling from the emanations after the discharge of the α-particle, has nothing to do with the charge carried at the instant of formation, but depends entirely on the character of the gas molecules encountered during the recoil.[31] In dry air, all the particles of active deposit remain positively charged, whereas in an atmosphere of pure ether vapour, and probably in pure water vapour, all remain uncharged. In a mixture of air and vapour, the proportion of charged to uncharged atoms depends on the proportion of air and vapour in the mixture. Hydrogen, oxygen, and carbon dioxide all behave like dry air in this respect, whilst ethyl bromide vapour resembles ether.

[31] G. H. Henderson, *Trans. Roy. Soc. Canada*, 1917, [iii], **10**, 151 ; *A.*, 1917, ii, 351 ; compare *Ann. Report*, 1916, 263.

As regards the distribution of the active deposit in an electric field, it has also been shown that the phenomenon of the electric wind has much to do with the results obtained.[32] Thus, when the electrodes consist of a sharp needle point opposite a disk and high potentials are employed, the electric wind drives the deposit on to the disk, independently of whether it is the cathode or the anode, provided that the gas is strongly ionised. This, for example, is usually the case when the experiment is made in a vessel much used with the radium emanation, and on the interior surface of which an active layer of polonium has formed. By suitably arranging the electrodes, the electric wind may cause a continuous circulation of the gas round a closed annulus. If into the gas a strong source of radium-A is introduced, radium-B particles, recoiling from it and becoming discharged, remain in the gas without depositing. These uncharged radium-B particles may be caused by the electric wind to go on circulating in the apparatus long after the radium-A that gave rise to them has all disintegrated, and may be made to deposit at will by directing them to a surface by the electric wind independently of the sign of the charge on the surface. Similarly, the motion of the so-called large ions in the electric field is to be ascribed to the electric wind, and not, as formerly supposed, to their carrying an electric charge.

Another curious and as yet unexplained property of the radium active deposit is that, after it has been deposited on a disk, it spreads to a slight extent to surrounding surfaces, as if slightly volatile.[33] Thus, if a plate is mounted opposite to the disk coated with the active deposit, the plate being positively charged with reference to the disk to avoid radium-B from being deposited on it by recoil in the case that radium-A is present in the active deposit, the plate always acquires a small fraction of the same active deposit as is present on the disk. This proportion is much decreased by washing the deposit on the disk or by gently heating it, but is not much affected by the physical or chemical condition of the surface of the disk or by directing on the coating of active deposit a violent blast of air. When the exposure of the disk to the emanation has been short, the proportion of active deposit lost in this way is much increased, and, for exposures of only a few seconds, it may become comparable with the amount of radium-B lost by recoil. The phenomenon constitutes a very insidious source of possible error in certain experiments. For example, the recoil of radium-C_2 may be entirely masked by it if precautions are not taken. A very remarkable point is that, from radium-A, the

[32] S. Ratner, *Phil. Mag.*, 1917, [vi], **34**, 429 ; *A.*, 1917, ii, 558.

[33] *Ibid.*, 1918, **36**, 397 ; *A.*, ii, 419.

quantity escaping from the disk diminishes in a regular manner with lapse of time, falling to half the initial value in 1·4 minutes, though the half-period of radium-A itself is three minutes. Although no explanation is advanced, the practical importance of the effect has to be borne in mind.

Various.

Solubility of Pure Radium Sulphate.—It is a strange but seemingly well-established fact that, when a barium–radium solution is precipitated by sulphuric acid or a soluble sulphate, there is no change between the relative concentration of the radium and barium in the fractions precipitated and left in solution, even when the precipitant is in excess. The behaviour, which has been termed " pseudo-isotopy," resembles that of two isotopic elements, although barium is easily separable from radium.[34] It suggests that the solubilities of radium and barium sulphate are the same, and this point has been investigated. The solubility of barium sulphate in water at 25° is $2·3 \times 10^{-6}$ gram per c.c. A rough extrapolation from the solubilities of the sulphates of calcium, strontium, and barium to that of radium sulphate indicates, for the latter, a solubility of the order of 10^{-8}. In the practical working up of carnotite for radium, however, by the precipitation of solutions of radium, in the presence of a million-fold its weight of barium, by sulphuric acid, only some 10^{-11} gram of radium per c.c. is contained in the solution.

The direct estimation was carried out by the fractionation of some 0·25 gram of radium in the form of bromide to 100 per cent. purity, which was checked by a comparison with the U.S.A. substandard. This was converted into the sulphate, and the solubility at 25° determined for 1 c.c. of the solution by the emanation method, in pure water and in various concentrations of sulphuric acid. The values obtained, between 2·0 and 2·3 ($\times 10^{-8}$ gram per c.c.), were constant in pure water and in sulphuric acid up to 50 per cent. concentration, but rapidly increased with higher concentration, being twelve times as great for 70 per cent. as for 65 per cent. concentration. The constancy of the solubility for low concentrations of sulphuric acid is notable. The case is one of the clearest and most striking of that sharp chemical behaviour of radioactive substances in infinitesimal quantity in the presence of an analogous element which has been so frequently remarked, and has made the practical chemistry of these substances so vastly

    [31] S. C. Lind, J. E. Underwood, and C. F. Whittemore, *J. Amer. Chem. Soc.*, 1918, **40**, 465 ; *A.*, ii, 144.

easier than could have been anticipated. On thinking over the matter, the explanation that suggests itself is that radium and barium sulphates are isomorphous and constitute in the solid state a single phase rather than two phases.

Series Spectrum of Radium.—There is no doubt that the atomic number rather than the atomic weight is the constant controlling most nearly the chemical and spectroscopic character of the elements, and many approximate relations found to hold for the atomic weight have been re-examined for the atomic number. By plotting the logarithms of the frequency differences between the extreme members of the triplets in the spectral series of the elements of the second family against the logarithms of the atomic weights, the alternate members have been found to fall on two straight lines, the one comprising mercury, cadmium, zinc, and magnesium, and the other barium, strontium, and calcium. By extrapolation, the frequency difference found for radium is approximately 3060 Å. In the radium spectrum there are a number of triplets with average frequency differences 2016·64 and 1036·15, and there is little doubt that the sum of these, 3052·79, is a characteristic of the radium spectrum, although the conclusion still had to be confirmed by magnetic resolution of the lines to ascertain the series to which they belong.[35]

Technical Extraction of Radium from Carnotite.—Some further particulars are given of the results of tests on the working up of carnotite by treatment with concentrated sulphuric acid, or fusion with sodium sulphate, and fractional sedimentation of the product after lixiviating with water, that have already in part been described.[36] Allowing the coarse and finer sediments to settle separately, 87 per cent. of the contained radium was present in the latter, in which the radium was from twenty to thirty times more concentrated than in the original ore. The sediment consisted of 90 per cent. of sand and 10 per cent. of sulphates, and a further concentration of the radium from 150 to 300 times was effected by solution in boiling concentrated sulphuric acid and reprecipitation with water containing a trace of barium chloride, or by fusion with sodium carbonate, and proceeding as in the more usual method.

"*The Milligram of Mesothorium.*"—A technically very important quantity, and one that, by its nature, has proved difficult to connect

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[35] Gladys A. Anslow and Janet T. Howell, *Proc. Nat. Acad. Sci.*, 1917 **3**, 409; *A.*, 1917, ii, 401. Compare also H. Bell, *Phil. Mag.*, 1918, [vi], **36** 337; *A.*, ii, 383.

[36] A. G. Loomis and H. Schlundt, *J. Ind. Eng. Chem.*, 1916, **8**, 990; *A.*, 1917, ii, 31. Compare *Ann. Report*, 1916, 269.

with other radioactive quantities, is the so-called milligram ·of mesothorium, meaning, thereby, the quantity of mesothorium-1 and -2 in equilibrium (actually, of course, unweighable) which·has the γ-ray activity of 1 milligram of radium (element) in equilibrium with its first four products and in the form of any convenient compound. In a long and difficult investigation into the relative contribution of the various members of the disintegration series of thorium to the radioactivity of thorium minerals, it was found that the quantity in question was that in equilibrium with 19 kilograms of thorium in thorium minerals, the γ-rays being measured through 2 mm. of lead and 1·32 mm. of brass. Therefore 1 gram of thorium in its minerals is in equilibrium with $0·524 \times 10^{-4}$ "milligram of mesothorium," whereas 1 gram of uranium in its minerals is in equilibrium with $3·24 \times 10^{-4}$ milligram of radium. Thus, to obtain preparations of the same γ-activity, which is the basis on which they are sold, six times as much thorium as of uranium has to be worked up, which indicates sufficiently the relatively unfavourable position of the thorium minerals compared with those of uranium as sources of radioactive preparations, and to some extent discounts the advantage that in the case of the thorium the raw material is an otherwise valueless by-product.[37] In the same work it was concluded that, of the γ-activity of ·a thorium mineral due to thorium, 36·3 per cent. was derived from mesothorium and 62·7 per cent. from radiothorium, or, speaking more strictly, from mesothorium-2 and from thorium-D respectively.

Life-periods of Thorium, Mesothorium, and Radiothorium.—The period of radiothorium, according to a consensus of independent evidence, is somewhat less than that formerly accepted. The most careful and accurate determination[38] gives 1·905 years, or 696 days, for the period of half-change, or 2·75 years for the period of average life, with a probable accuracy within 1 per cent.

For the period of mesothorium-*I* a value was found, namely, 6·7 years, much higher than that, 5·5 years, usually accepted for the half-period. The new value, which was confirmed in independent experiments and seems thoroughly well founded, makes the period of average life 9·67 years, the period for the maximum α-radio-activity of a mesothorium preparation due to the growth of radio-thorium, 4·83 years, and the maximum for the γ-rays 3·34 years. For preparations of equal α-activity of (1) radium, (2) radio-thorium, (3) mesothorium in equilibrium with accumulated radio-

[37] H. N. McCoy and L. M. Henderson, *J. Amer. Chem. Soc.*, 1918, **40**, 1316 ; A., ii. 422.

[38] L. Meitner, *Physikal. Zeitsch.*, 1918, **19**, 257 ; A., ii, 347 ; compare B. Walter, *ibid.*, 1917, **18**, 584 ; A.,.;ii, 51.

thorium. the γ-activities are in the ratio $1.00:0.66:1.11$. For the period of thorium itself, a higher value than is usually accepted was found by a long and somewhat indirect method. The half-period found was 2.37×10^{10} years, assuming that radium to be 1740 years, as compared with previous values ranging from 1.28 to 1.86 ($\times 10^{10}$ years).

The Decay of Luminosity of Radium–Zinc Sulphide Paint.—The increasing use of radium luminous paint in watches, compasses for night flying, and the dials of instruments generally, has made the question of the decay of the luminosity, due to the deterioration of the zinc sulphide exposed to the α-ray bombardment, of great practical importance. A description has been given of the methods employed at the National Physical Laboratory for testing the luminosity of luminous preparations, both before and after application to the dials of instruments, of the considerations governing the choice and specification of these preparations and of the instrument with which they are used, and of the decay of the luminosity with time. Through some effect of the medium used to fix the preparation on to the surface coated, probably in protecting the zinc sulphide to some extent from the α-ray bombardment, the rate of decay of the luminosity of the compound is only from one-third to one-fourth as rapid, after the paint has been applied, as it is before application.

On Rutherford's theory of the destruction of " active centres ' in the zinc sulphide by the bombardment, the luminosity should decrease to zero exponentially with the time. In practice, it is found that, whilst this is true for the initial period, some 200 days from manufacture, the rate of decrease then falls off and the luminosity then tends to approach a limiting value which is not zero.[39] A modification of the theory to account for this, that there is a recovery of the destroyed active centres at a rate proportional to their concentration, has been proposed and found to agree with the experimental results in the case of eight different samples examined. The expression connecting the brightness. B_t, at any time from preparation, t, with the time, t, is $\log(B_t - m) = kt$, where m and t are constants. One conclusion of the work, which is of practical importance, is that no advantage commensurate with increased cost is gained by increasing the radium content above 0.2, or at most 0.3 milligram of radium per gram of zinc sulphide. For fuller results of the decay of these preparations, the original papers should be consulted.

[39] C. C. Paterson, J. W. T. Walsh, and W. F. Higgins, *Proc. Physical Soc. London*, 1917, **29**, 215. J. W. T. Walsh, *Proc. Roy. Soc.*, 1917, [A], **93**, 550 ; *A.*, 1917, ii, 559.

Effect of Radium Rays on Colloids.—Using preparations of radium containing 0·1 gram of the element, some remarkable results have been observed of the effect of the β- and the γ-rays·on the colloidal solution of ceric hydroxide, prepared by dialysing a solution containing 10 per cent. of ceric ammonium nitrate. This solution, left to itself, ages with time, in that its viscosity decreases, and its liability to coagulate and its sensitiveness to electrolytes diminish. These spontaneous changes, which are attributed to gradual dehydration of the colloidal particles, are accelerated by rise of temperature and are not reversible. Exposure to the β- or γ-rays of radium at first accelerated the diminution of viscosity. but, after that, the viscosity steadily increased to a very high value, and after many days a stable, clear jelly resulted. Once the increase of viscosity has set in, it appears to proceed independently as to whether exposure to the rays be continued or not. If, however, the irradiation is terminated before the initial diminution of viscosity is completed, the viscosity rises abruptly, reaches a maximum, and then decreases almost as abruptly until a value near the minimum is reached. A fresh exposure to the radiation, after quickly completing the reduction of the viscosity to the minimum that would have been reached by constant irradiation, then gelatinises the solution with relatively great rapidity. The curve connecting the viscosity and the time, as regards the abrupt rise to a maximum followed by the fall to a minimum value, is reminiscent of the type familiar in radioactive change, such, for example, as would be obtained for the variation of the activity with the time in the case of a radioactive substance, not itself giving rays, but producing a product, of period similar to its own, responsible for the radiation. The agent used, owing to the magnitude of the effects and the apparent regularity with which they occur, seems to be one well suited for the study of effects of this character, and the results look as if they should be amenable to strict mathematical interpretation. The effects of the rays are, in general, similar to those produced by minute traces of electrolytes in amount insufficient to produce immediate coagulation. They differ, however, in detail. For example, with electrolytes, the initial reduction of viscosity occurs instantaneously, and the jelly finally produced is unstable.[40]

The explanation of Zsigmondy,[41] that the colloidal state of the active deposits in neutral and alkaline solutions, recognised first by Paneth, may be due to the adsorption of the radio-elements by

[40] A. Fernau and W. Pauli, *Kolloid Zeitsch.*, 1917, 20, 20; *A.*, 1917, ii, 189.
[41] *Ann. Report*, 1913, 275.

xisting colloid particles in the liquid, possibly derived from the 'lass containing vessels, has been criticised as inadequate, and urther.experiments carried out on the properties of the radium ctive deposit in various solvents.[42] The proportions of the active eposit obtained on the anode and cathode respectively, and the adsorption of the radioactive substances by various adsorbents, were both found to depend to a considerable extent on the nature of the solvent.

Pleochroic Halos.[43]—A careful study of the appearance and dimensions of the pleochroic halos found in various kinds of mica has raised many new problems. Although the final stage of the halo corresponds with what might be expected, the early stages of development, in which concentric rings appear, corresponding in radius with the ranges of the various α-particles concerned, are extremely difficult to explain. Because the outward spreading of the rays, according to the square of the distance from the centre, ought so to weaken the darkening at the edge, relatively to that at the centre, that the "corona" due to radium-*C* ought never to appear before the centre has blackened up, whereas this corona is a well-marked feature in the early stages of development of the halo. In fact, the development is almost exactly what would be expected for a parallel beam of α-rays rather than for rays proceeding ·outward from a point source. To account for this, Joly assumes that the more quickly moving α-rays, which reach to the edge of the halo, in their passage through the mica can reverse the effect of the more slowly moving rays, much as the latent image in the photographic plate caused by *X*-rays may be reversed by subsequent exposure to light. Whatever the explanation, there is no doubt of the fact that the halos do develop in a regular sequence, the first effect being the appearance of the central sphere due to the rays of short range, followed quickly by the appearance of the outer concentric rings due to the rays of longer range. The mica from a Vosges granite was found to be very rich in thorium halos, which, under the microscope, can readily be distinguished by their dimensions from the more common uranium halos, abundant in the mica from the Leinster granite of County Carlow and from Ballyellen. In addition, one clear example of a mixed uranium—thorium halo was found, together with another class of halo, ultimately traced in its origin to the radium emanation by means of its dimensions. The latter were found in conduits in the mica,

[42] L. Zachs, *Kolloid Zeitsch.*, 1917, **21**, 165; *A.*, ii, 95.

[43] J. Joly, *Phil. Trans.*, 1917, [A], **217**, 51; compare *Ann. Report*, 1910, 260; 1913, 279.

through which water charged with radium emanation presumably had percolated, around some nucleus capable of adsorbing or retaining the emanation.

A very careful and accurate series of measurements of the radii of the component features of all these halos gave results that agreed perfectly with the known ranges of the α-rays and the stopping power of the mica, except in one very significant case.

Whereas the outer features of the uranium halo exhibit good correspondence, the inner features undoubtedly do not fit, the central portion being distinctly larger in radius than is to be expected from the range of the rays concerned in its production. In attempting to account for this, Joly advances the suggestion that the period of uranium may have been shorter, and the α-rays expelled therefore longer in range, in former geological times than is now the case. For the case of the thorium halos, there is no reason to believe that the transformation has not proceeded throughout at a uniform rate. The view, in the case of uranium, would also serve to reconcile the discrepancy between the radio-active and geological estimates of the age of the earth from the lead-uranium ratio of minerals. It is clear that before a suggestion so completely at variance with what must be regarded as a fairly well-founded conclusion can be accepted, much stronger and more definite evidence will have to be put forward.

Scattering of α-Particles by Gases.—A method has been described for determining the scattering of α-particles in gases, especially in hydrogen, by passing the α-rays from a fine needle point, coated with the active deposit, through a small hole and receiving them on a photographic plate at a suitable distance in an apparatus that can be filled with the desired gas at suitable pressure. The number of darkened silver grains in the photographic image can be counted under the microscope, and since the number of grains, in general, is proportional to the number of α-particles, the method can be used for determining the deflections suffered by the α-particle in its passage through the gas. So far, only preliminary results have been obtained.[44]

Bismuth Hydride.—A problem of chemistry that has been previously much investigated without definite result, whether bismuth forms a volatile hydride analogous to the compounds formed by the other elements in this family, has been the occasion for an elegant application of the conversion of a chemical into a radioactive problem by the use of a radioactive isotopic element. The C-members of the disintegration series are isotopic with

[44] R. R. Sahni, *Phil. Mag.*, 1917, [vi], **33**, 290 ; compare *Ann. Report*, 1916, 261.

bismuth, and, in the present case, thorium-C' was chosen. Magnesium foil coated with the active deposit of thorium was dissolved in acid and the evolved hydrogen passed into an electroscope, as in testing for an emanation. The gas showed distinct radioactivity, which was identified with that of thorium-C by its rate of decay. The general behaviour showed that the activity was almost certainly due to a gaseous compound, and not to the mechanical carrying over of a spray of the liquid. Its rate of spontaneous decomposition was investigated. At the ordinary temperature in an atmosphere of hydrogen, 20 per cent. remained undecomposed after fifty minutes, but at higher temperature dissociation proceeded much more rapidly. Only 6 to 7 per cent. remained on passing through a tube heated to 350°. If the tube was heated to redness at one point, complete decomposition occurred with the sharp deposition of thorium-C just beyond the heated portion, exactly as in Marsh's test for antimony. The gas could be condensed by liquid air, and, by the use of strong preparations, it was possible to establish that a small fraction revolatilised when the liquid air was removed. It is hoped that the experience gained as to the best conditions for its formation will lead to its becoming possible to put into evidence the formation of ordinary bismuth hydride by chemical or microchemical methods.[45] The research is analogous to that previously reported on a volatile hydride of polonium.[46]

Nomenclature of the Radio-elements.—But for the war, the nomenclature of the radio-elements would have been discussed at the International Congress, proposed to be held in Vienna in 1915. In the meantime, a nomenclature has been provisionally adopted by the German and Austrian investigators, and used in the treatise on radioactivity by Meyer and von Schweidler.[47] As regards the symbols, isotopes are indicated by Roman, successive products by Arabic indices, thus: U_I, U_{II}; $MsTh_1$, $MsTh_2$; UX_1, UX_2; the name uranium-Y is retained for the branch product at the head of the actinium series, but for the branch products of the C-members, one dash indicates the isotopes of polonium and two dashes the isotopes of thallium. Thus we have ThC', RaC', AcC', indicating the members usually so designated, but ThC'', RaC'', and AcC'' for what are usually known as Th-D, Ra-C_2, and Ac-D. Radium-D retains its present significance, but the names thorium-D

[45] F. Paneth, *Zeitsch. Elektrochem.*, 1918, **24**, 298; further details have been published too late for inclusion here (*Ber.*, 1918, **51**, 1704, 1728).

[46] *Ann. Report*, 1916, 266.

[47] S. Meyer and E. von Schweidler, *Zeitsch. Elektrochem.*, 1918, **24**, 36; *A.*, ii, 94; compare K. Fajans, *ibid.*, 1917, **23**, 250; *A.*, 1917, ii, 523.

and actinium-D are given to the products, respectively, of actinium-C'' (the main product) and of thorium-C' in the major branch. Fajans, on the other hand, somewhat earlier, proposed meantime retaining the names first given by the discoverers, and this is the plan adopted for the most part in the accompanying figure.[48]

Natural Radioactivity.

Radioactivity of the Atmosphere.—The height in the atmosphere to which the various radioactive gases and their products may be expected to extend has been the subject of inquiry. Owing to the decay of the radioactive substance which is supplied from the soil, its quantity will decrease with the height from the surface of the earth the more rapidly the shorter is its period of average life. The heights in which the quantities may be expected to be reduced to one-half of the value at the surface are: for the radium emanation and its short-lived products, 1200 metres; for thorium-B and its short-lived products, 100 to 150 metres; for actinium-B and products, 10 to 20 metres; for thorium emanation and thorium-A, 2 to 3 metres; and for actinium emanation and actinium-A, 0·5 to 1 metre. The distribution of radium-D and products should be essentially uniform up to a height of 10 kilometres. So far as experimental evidence, from balloon ascents, is available for the case of the radium emanation, the calculated distribution with height appears to be borne out. On this basis, the total quantity of radium emanation in the whole atmosphere is calculated to be about 2×10^7 curies, or the quantity in equilibrium with some 20 tons of radium (element).[49]

A study of the quantity of the radium emanation in the atmosphere at Freiburg, Switzerland, extending over several years, gave for the mean content 131, with a maximum of 305 and a minimum of 54 ($\times 10^{-18}$ curie per c.c.), which is somewhat higher than the values previously found in other localities. As elsewhere, the quantity was found to vary in a more or less regular manner with the meteorological conditions.[50]

Radioactivity of Rocks.—A radioactive survey of the Archæan complex of Mysore State, S. India,[51] affords an interesting example

[48] Compare also C. Schmidt, *Zeitsch. anorg. Chem.*, 1918, **103**, 116; *A.*, ii, 305.

[49] V. F. Hess and W. Schmidt, *Physikal. Zeitsch.*, 1918, **19**, 109; *A.*, ii, 213.

[50] J. Olujić, *Jahrb. Radioaktiv. Elektronik*, 1918, **15**, 158; *A.*, ii, 420.

[51] W. F. Smeeth and H. E. Watson, *Phil. Mag.*, 1918, [vi], **35**, 206; *A.*, ii, 96.

of the independent evidence afforded to the petrologist by radio-activity in dealing with the complicated problem of classifying and correlating the members of a highly metamorphosed and confused mass of rocks. The oldest rocks, epidiorites and hornblendic schists of the Dharwar system, are low and uniform in radium content, between 0·14 and 0·25 ($\times 10^{-12}$ gram per gram), and the next in age, the rocks of the Chloritic series, do not much differ from them. The intrusions of the Champion gneiss and the related quartz veins of the Kholar field contain much more radium, whilst the basic intrusions of Dharwar age contain much less radium than the schists themselves. The next oldest rocks, the Champion gneiss, Peninsular gneiss, and Closepet granite, contain some four times as much radium as the Dharwar schists and some twelve or fifteen times as much as those next following in order of age, the Charnockites, which stand quite apart in their very low radium content, and which Holland had previously classified as a distinct petrographical province. These very ancient rocks, which are all presumably of igneous origin, contain, in general, remarkably little radium, the more basic less than the more acidic, as is usually found, except for the Charnockites, which are of intermediate chemical composition. In the Kolar field, where the schists are fairly uniform, no increase in radium content occurs with the depth below the surface.

The examination of a Sardinian porphyritic granite showed that its radioactivity, which was traced to the presence of uraniferous biotite, had probably been acquired by the action of percolating water that had previously traversed strata containing uranium minerals.[52] A number of other Italian minerals have also been examined.[53]

Meteorites.—An investigation of the radioactivity of twenty-two meteorites showed that the metallic meteorites are practically free from radium, and that the stony meteorites contain, on the average, less than one-fourth of the radium contained in an average granite.[54]

Radioactivity of Natural Waters.—A detailed and prolonged examination has been made into the radioactivity of the natural waters of a very small area in the Neuchâtel Jura mountains, without disclosing any inter-connexion between the radioactivity, which in all cases was small, and the volume of flow, temperature, and

[52] A. Serra, *Gazzetta*, 1917, **47**, ii. 1; *A.*, ii, 348.

[53] L. Francesconi, N. Granata, A. Nieddu, and G. Angelino, *ibid.*, 1918, **48**, i, 112; *A.*, ii, 421.

[54] T. T. Quirke and L. Finkelstein, *Amer. J. Sci.*, 1917, [iv], **44**, 237; *A.*, 1917, ii, 576.

chemical composition of the springs.[55]   There were a few thermal and mineralised springs in the region examined, but they were not specially radioactive.   The radioactivity of the springs increased in passing across the Jura chain in the direction from S.E. to N.W., and, travelling in this direction, the crystalline rocks beneath come nearer to the surface.

Several investigations have been made of the radioactivity of the waters in the Philippine Islands.   The sea-water from Manila Bay, in the China Sea, was found to contain a quantity of radium, from 0·2 to 0·1 (× 10⁻¹² gram of radium per litre), much lower than has been found for sea-water from other parts of the world.[56] The waters of some ninety springs in the Philippine Islands contained radium emanation from 21 to 13 (× 10⁻¹⁰ curie per litre), but no dissolved radium.[57]   In the mountainous region of northern Luzon, which shows evidence of recent vulcanism, and where salt and hot springs are numerous, no highly radioactive waters were encountered.[58]   One spring was examined over long periods of time, during which great variations in the volume of flow took place, but the emanation content of the water remained remarkably constant.

<div style="text-align: right">FREDERICK SODDY.</div>

[55] H. Perret and A. Jaquerod, *Arch. Sci. phys. nat.*, 1918, [iv], **45**, 277 ; 366, 418 ; A., ii, 255.

[56] J. R. Wright and G. W. Heise, *Philippine J. Sci.*, 1918, **13**, [A], 49 ; A., ii, 420.

[57] *Idem, J. Physical Chem.*, 1917, **21**, 535 ; A., 1917, ii, 560.

[58] G. W. Heise, *Philippine J. Sci.*, 1917, **12**, [A], 293, 309 ; A., ii, 182.

INDEX OF AUTHORS' NAMES

INDEX OF SUBJECTS